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THE VIBRATION-ROTATION SPECTRUM OF AMMONIA GAS AT 3μ

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A number of investigations have been made on the structure of the double branched absorption bands in the near infra red spectrum of some simple diatomic molecules. The excellent work of Imes[1] gives the results of measurements for the diatomic hydrogen halides HCl, HBr, and HF. Other investigators have reported the existence of double branched bands for polyatomic molecules, notably that of water vapor by Sleator.[2]

The later theory bearing on the origin of those bands has been quite satisfactorily developed for the diatomic molecule by Lenz[3] and Kratzer.[4] No success has been reported thus far for the theory of bands exhibited by polyatomic molecules. Though the problem for the polyatomic molecule has resisted a quantitative solution, it would appear qualitatively that such a molecule must have axes of vibration and also of rotation and that the absorption of radiation is governed by changes of stationary states of vibration and rotation such as are assumed for the simple diatomic molecule.

During a study of ammonia gas, in an attempt to resolve the bands which were already known to exist, it was found that the band at 3μ was not simple but double with serrated branches similar to that of HCl. There is, however, a very notable difference between the ammonia band and that for HCl which is dealt with in the sequel.

[1] Astrophysical Journal, *50*, p. 251; 1916.
[2] Astrophysical Journal, *48*, p. 125; 1918.
[3] Verh. d. D. Phys. Ges. *31*, p. 632; 1919.
[4] Zs. f. Phys. 289, 1920.

EXPERIMENTAL PROCEDURE

The absorption of ammonia gas was studied by means of a grating spectrometer[5] and radiometer. The grating of 2500 lines per inch was kindly loaned to me by Professor H. M. Randall of the University of Michigan. The radiometer was similar to the one already described[6] with the exception of the vanes which in this instrument were made of aluminum leaf, .25 mm wide and 15 mm long, instead of phosphor bronze. The decrease in the moment of inertia of the system introduced by the use of aluminum leaf led to a much greater sensibility without an increase in the period.

An absorption chamber, 15 cm long with quartz windows, contained the ammonia gas. It was so arranged before the slit of the spectrometer that it could be withdrawn and replaced by two quartz plates equal in thickness to that of the absorption chamber windows, thus eliminating the absorption of these windows. Radiation was sent from a Nernst glower to a concave mirror, through the absorption chamber and focused upon the spectrometer slit. The slit width was .25 mm. The radiation from the slit was incident on a 60 cm concave mirror of 15 cm aperture. The parallel radiation reflected from this mirror was incident on the grating. The diffracted radiation of the first order at 3μ was returned to the mirror and thence on the radiometer vane. No auxilliary rock salt prism was used to disperse the radiation before its entrance to the spectrometer, because it was found that the shorter wave lengths of higher orders possessed practically no energy. The spectrometer was carefully calibrated by noting the angular deviation of the several orders of the sodium lines.

The ammonia gas was prepared by heating a mixture of pure CaO and NH_4Cl and drying it, by passing it through soda-lime towers. The gas was also obtained by warming concentrated chemically pure NH_4OH. The gas was then run into the cell at room temperature and at atmospheric pressure.

To obtain the percentage transmission of the gas the radiometer deflections, with the absorption chamber in place before the slit and then with the quartz plates in place, were obtained. The ratio gave the necessary percent transmission. Owing to the smallness of the absorption, it was necessary to repeat observations many times and to space them very closely to locate the maxima of absorption. Fig. 1

[5] J.O.S.A. & R.S.I., *7*, p. 853; 1923.
[6] J.O.S.A. & R.S.I. *6*, p. 625; 1922.

exhibits the character of the absorption. It is seen that the depth of the bands is not much in excess of 5% for the 15 cm. cell. The use of a longer absorption chamber was impractible owing to the rather large general absorption. In order to locate more accurately the points of

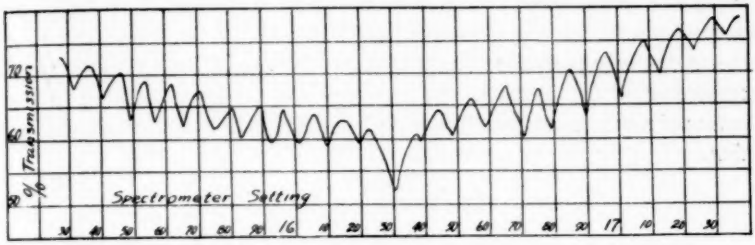

FIG. 1

maximum absorption, the spectral distribution as it passed through the absorption chamber was obtained. This allowed the use of radiometer deflections of the order of 400 mm. The selective radiation of the Nernst glower in this region tended to complicate matters. Fig. 2

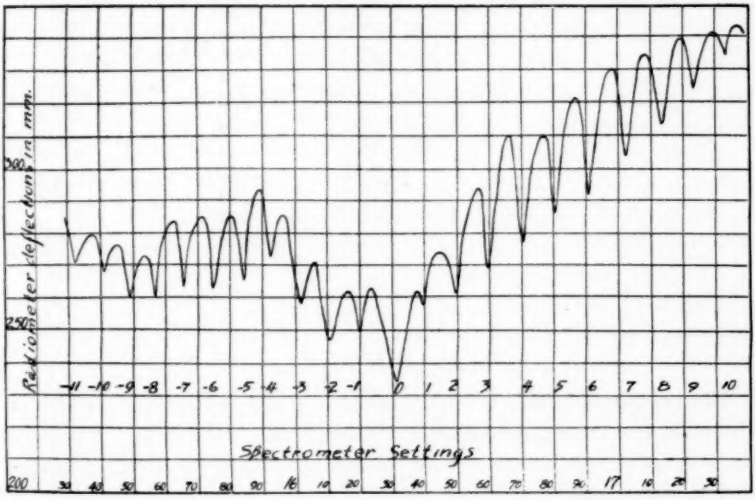

FIG. 2

shows the distribution after passage through the gas and indicates that the absorption is small but allows a more accurate location of the points of maximum absorption than does Fig. 1.

The wave lengths of the positions of maximum absorption are recorded in Table 1. The bands are numbered to the right and left from the central band. The table shows that the bands are not equally spaced, the wave length difference ranging from 140 A on the short wave side to the band to 200 A on the long wave side. There appears no uniform increase in the wave length difference. It is probable that this is due to experimental error owing to the insufficient resolution and dispersion of the grating. In any case the accurate location of the points of maximum absorption is rendered difficult by the weak absorption.

TABLE 1.

Band	Wave length in μ	Difference in μ
-11	2.8212	.0159
-10	2.8371	.0140
- 9	2.8511	.0160
- 8	2.8671	.0158
- 7	2.8829	.0153
- 6	2.8982	.0169
- 5	2.9151	.0166
- 4	2.9317	.0164
- 3	2.9481	.0167
- 2	2.9648	.0167
- 1	2.9815	.0207
0	3.0022	——
1	3.0166	.0144
2	3.0354	.0188
3	3.0547	.0193
4	3.0737	.0190
5	3.0924	.0187
6	3.1110	.0186
7	3.1318	.0208
8	3.1528	.0210
9	3.1719	.0191
10	3.1899	.0180

The graphs and table reveal the presence of a central band which is absent in the absorption of the hydrogen halides, the lack of which in these substances, though not out of accord with the theory, is nevertheless surprising.

DISCUSSION OF THE RESULTS

While it is interesting to find that the ammonia gas shows bands similar to the hydrogen halides, the existence of the central branch or so-called zero branch is significant. The theory developed by Lenz,

loc.cit. for the position of the points of maximum absorption for the diatomic molecule, assumes that the molecule is capable of harmonic vibration along a line between the atomic centres and a rotation about an axis through the centroid and at right angles to the axis of vibration. To obtain an expression for the location of the bands it is first necessary to determine the sum of the energies of vibration and rotation assuming that the molecule may exist in a series of stationary states n and m with respect to vibration and rotation respectively. By applying the Bohr frequency condition and allowing the stationary states to change in conformity with the Principle of Selection, we arrive at the expression,

$$\nu = \nu_0 + B(\pm M + 1)$$

for the frequency of the bands in terms of the oscillation frequency, ν_0, the state, m, characterizing the initial condition of rotation and a constant B. which involves h, and the moment of inertia, I, of the molecule, that is, $B = h/8\pi^2 I$. The expression implies an initial condition, $n = 0$, for the atomic oscillation. By giving m the series of values 1, 2, 3, 4, etc., we obtain a series of values for the frequencies of the equally spaced bands lying symmetrically on either side of a band whose frequency is determined by letting $m = 0$. The significance of $m = 0$ is important for it means that the molecule may exist in the rotationless state a fact which has not been borne out by the experiments on the hydrogen halides. In these substances the zero branch is absent. One also meets this situation in a consideration of the specific heat of rotation for water vapor.[7]

The equality of spacing, demanded by the theory, is not borne out experimentally. In cases examined thus far, it is found that the frequency difference between the bands continuously increases with decrease in frequency. Kratzer, *loc.cit.*, remedies this defect by assuming that for larger amplitudes of oscillation, the vibrations are non-harmonic and that the moment of inertia of the molecule is not constant. The consequences lead to the dependence of the stationary states n and m on one another, an unequally spaced series of bands, and the possibility of harmonics.

A glance at Fig. 1 reveals the fact that the bands are not equally spaced on either side of a central frequency, $\nu_0 + h/8\pi^2 I$, but that there is an increase in the frequency difference with decreasing band frequency. The presence of the zero branch corresponding to the fre-

[7] Ann. d. Phys., *58*, 682; 1919.

quency, $\nu_0+h/8\pi^2L$, is quite prominent and indicates that many of the ammonia molecules may exist in the rotationless state $m=0$.

The attempt was made to locate the harmonic band at 1.5μ. Such a band was found at approximately 1.5μ. It was double branched and very faint. The faintness and lack of energy in this region of the spectrum made it impossible to take accurate measurements on it.

NORTHWESTERN UNIVERSITY,
EVANSTON, ILLINOIS.
OCTOBER 1, 1924.

Attempt to Determine the Duration of the Metastable State in Mercury Vapor.—Between a filament and a grid Webb applied a voltage of the form $(4.9+x \sin nt)$, x being of the order 0.5 volt, so that mercury atoms near the grid could be knocked into a metastable state by impacts during the positive half-cycles, and not during the negative half-cycles. Between another grid and a plate, some distance away within the same tube, he applied a voltage of the form $y \sin nt$, so that photoelectrons excited from the grid would proceed to the plate during the positive half-cycles, and electrons excited from the plate would proceed to the grid during the negative half-cycles. Between grid and plate an electrometer was connected; this should show a positive current independent of frequency, if the mercury atoms emit their radiation instantaneously when they are knocked into the metastable state; while if emission occurs at an interval τ after excitation, it should show a positive current at low frequencies and a negative current at higher frequencies, eventually changing over again into a positive current. The observed dependence of electrometer current on frequency conforms to this latter description, indicating values for τ amounting to 1/3600 in one tube and 1/7600 second in another (a smaller) one. But the interpretation is not so simple as it would seem; were it so, the maximum negative current should be attained at the same value of frequency for the two tubes of different dimensions, which is far from true; also the calculated values for τ seems much too large when compared with values deduced by other methods. Nor can the results be explained by supposing that individual quanta of radiation stop over with several atoms in succession before they reach the photosensitive electrodes, for this assumption leads to laws of dependence of electrometer-current on pressure and dimensions of tube, which are contrary to experiment. And if it be assumed that the originally excited atoms themselves transport the quanta to the region between the photosensitive electrodes before letting them go, the dependence on the dimensions of the tube is correctly given but the dependence on pressure is still discordant.—[H. W. Webb, Columbia; Phys. Rev. (2) *24*, pp. 113-128; 1924.]

KARL K. DARROW

THE ABSORPTION SPECTRUM OF VISUAL PURPLE

By William Mayo Venable

The absorption spectrum of visual purple from the eyes of monkeys and rabbits is represented by the full line in the accompanying figure. The points plotted are from data by Koettgen and Abelsdorf, as reviewed by Hecht.[1] I have assumed that this curve is made up of three curves, one of which has its maximum at .5μ, and that these component curves are symmetrical. This is what we should expect in the absence of reasons for finding the curves distorted. The curve designated *White* is so drawn, assuming a maximum at the crest of the absorption curve, with the full line on the left for a guide. Deducting the ordinates of this *White* curve from those representing the observations, there is indicated definitely a secondary maximum about .53μ and another at .675μ. These three curves are so drawn that their ordinates have a sum equal to the ordinates of the curve representing the observations.

In another connection I have shown that the brightness of the spectrum is due to the excitation of sensations of white, yellow and green, the qualities blue and red diminishing, rather than increasing the total brightness.[2] Continuing that study I have located more accurately the wave lengths that, at the least intensities, stimulate the recognizably different spectral hues, as follows: violet 443, indigo 462, blue 496, white 507, green 535, orange 611, red 632 mμ. The blue and the white maxima are quite close together. Inspection of the curves here submitted shows that it is not improbable that the visual purple examined and represented in the figure absorbs selectively that radiation that is most effective in producing the brightness sensations, white, yellow and green.

At first glance, it seems as if the inference might be drawn that the visual purple consists of three chemically separable substances, having different absorption maxima. This assumption, however, is not necessary, and is in conflict with what is known of the chemistry of the visual purple, which, however, is not very much. The unequal absorption may be due to the physical condition of the material, rather than its

[1] "The Visibility of Monochromatic Radiation and the Absorption Spectrum of Visual Purple," Selig Hecht and Robert E. Williams, Journ. Gen. Phys. *5*, No. 1; Sept. 1922; also J.O.S.A. & R.S.I., *9*, p. 221; 1924.

[2] "Color and Luminosity," Am. Journ. Phys. Opt., Jan. and April, 1924.

chemical composition, in the usual sense. In the retina the visual purple is very intimately associated with the terminal nerve cells, and the optic nerve is, normally, at a potential different from that of the surrounding tissue. This potential difference increases, by the action of

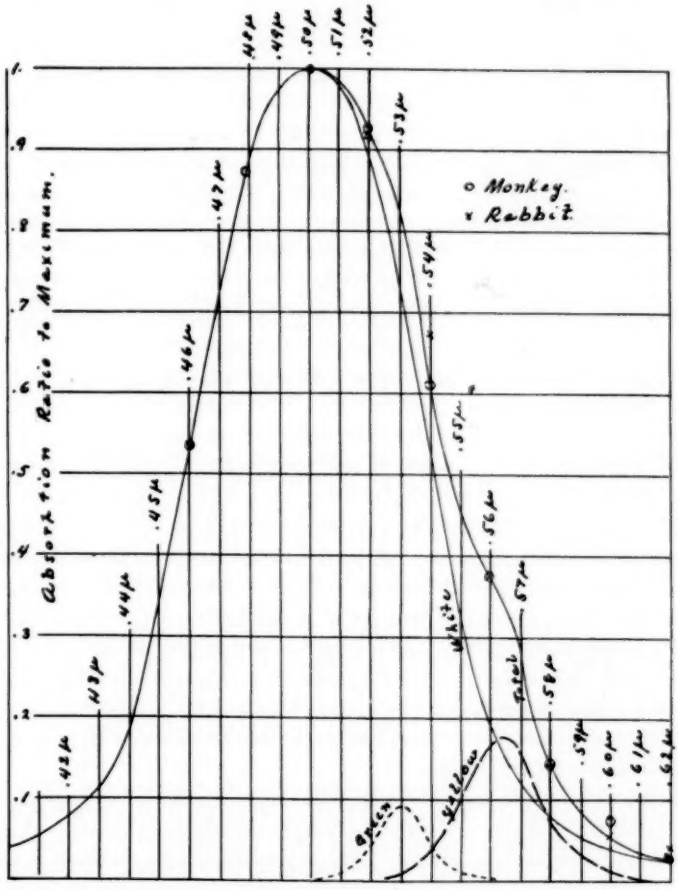

FIG. 1.—*Absorption Spectrum of Visual Purple.*

the nerve, when the retina is exposed to light, and undoubtedly tends to render the visual purple more sensitive to certain wave lengths than to others. It is generally believed that the visual purple is constructed in large molecules, made up of similar parts, and capable of occurring

in different degrees of aggregation,—that is, the parts capable of forming larger or smaller molecules, according to the circumstances.

The writer will be greatly obliged to anyone who may be able and willing to supply him with any data relating to the chemistry of the visual purple, or to its absorption spectrum after partial bleaching by light taken from any one part of the spectrum.

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Distribution in Direction-of-emission of Electrons ejected from Atoms by quanta.—Further experimental work upon this popular problem, in which the common scheme of using the C.T.R. Wilson method and estimating visually the angle between the path of the x-rays and the direction of emission of the electron is discarded, and a point-discharge ion-counter is used instead. A screen pierced by a slit intervenes between the ion-counter and the portion of the gas which the x-rays traverse; the counter is revolved around an axis collinear with the slit, and, when fixed at a particular azimuth θ, receives only such electrons as pass through the slit in directions inclined at θ to the x-ray beam, and hence depart from their atoms in directions similarly inclined; the curve of number of ions counted per second by the ion-counter, plotted versus θ, simulates the curve of number of electrons ejected versus angle of ejection. This at least should be true in the limit, when the density of the gas is made so low that electrons very rarely suffer deflections in passing from the place of origin into the ion-counter. It is hoped that this limiting state is approximately reached before the gas becomes too rarefied to produce electrons enough to measure. The observations were made on air and on gases the molecules of which contain I, Br, and Cl atoms respectively. The voltages of the tube generating the x-rays ranged from 25 to 60 kv.; the rays unfortunately are heterogeneous, as seems to be necessary to obtain sufficiently intense ones. The general result,—confirming all previous work—is that more electrons are expelled at angles $<90°$ (forward) than at angles $>90°$ to the primary beam; and the relative excess of forward-moving ones is greater, the higher the frequency. In assessing the advance over previous work it should be remembered that in measurements on incidence and emergence radiation from solids, there is no assurance that the electrons depart from the solid in directions approximating those in which they departed from the atoms. In this respect, however, Bothe's method is liable to be inferior to Wilson's. The excess of forward over backward expulsions also seems to be less for heavier halogen atoms than for lighter ones.

Bothe's theory is essentially that a quantum vanishes when it hits an electron, communicating its entire energy and momentum to it; if the electron is initially at rest, these two conditions prescribe the direction in which it flies away, which is inclined at $\theta_0 = \arccos \sqrt{h\nu/mc^2}$ to

the direction of the primary beam. The value of Θ_0 amounts to some 70°-80° for x-rays of various ordinary wave lengths. Bothe's explanation for the wide range of values of Θ actually observed is, that the orbital velocity of the struck electron is compounded with the velocity which a resting electron would acquire from the quantum. Specific assumptions are made about the interaction; but the agreement between predictions and experiment is not good, even the author describing it as "kaum schlechter als zu erwarten."—[W. Bothe, Reichsanstalt; ZS. f. Phys. *26*, pp. 59-84; 1924.] KARL K. DARROW

Fine Structure at and near X-ray Absorption Edges.—The absorption spectra of various salts (chiefly the higher and lower oxides) of the elements 22Ti, 23V, 24Cr and 25Mn are photographed in the neighborhood of the *K* absorption-frequency, and those of various salts of 50Sn, 51Sb, 52Te and 53L are photographed in the neighborhood of the L_{III} absorption-frequency. A few photometer curves made from the photographs are reproduced. The chief features of the photographs are: the absorption edge, which is always present; a narrow absorption line of greater wave length (a few X-units greater) than the absorption-edge, which is present when the metal or metalloid is combined with an exceptionally large number of oxygen atoms; and maxima and minima in the absorption coefficient at wave lengths somewhat smaller than that of the absorption edge. The absorption edge for a given element moves towards greater wave lengths as one passes from higher to lower oxides and finally to the element itself, but never (except possibly in the case of iodine) shifts as far over as the wave length of the absorption line. The smallness of these shifts suggests that the observed absorption frequencies are not far removed from those which atoms would display. Coster offers simple plausible interpretations of the three features of the fine structure, but no especial evidence for any of them.—[D. Coster, Haarlem; ZS. f. Phys. *25*, pp. 83-98, 1924.] KARL K. DARROW

X-ray Diffraction Fringes.—Repetition of the earlier attempts to detect diffraction fringes on a photographic plate exposed to a beam of x-rays beyond a wedge shaped slit. The experiments are carried out with rays from a Cu anticathode, which in the calculations are assumed to consist entirely of *Kα* radiation (wave length 1.54A); slight modifications were made in the technique to improve the results. Where the slit was less than 4.5μ wide, first order diffraction fringes were seen on the plate, one on each side of the direct image; where it was 5 to 6μ wide fringes of the second order were seen. The photographs reproduced in the article show these fringes fairly well; one must follow the author's advice to raise the plane of the paper almost to the eye and look along the line of the direct image. The agreement between observed and calculated values of the fringe-to-fringe distance is fair, probably as good as could be expected.—[B. Walter, Hamburg; Ann. d. Phys. *75*, pp. 189-194, 1924.] KARL K. DARROW

THE ILLUSION OF DEPTH FROM SINGLE PICTURES

By A. Ames, Jr.

Stimulated by a very interesting paper by Strieff[1] in which he describes and discusses Claparade's "paradox monokulare Stereoskopie," i.e. the greater illusion of depth we get by viewing a picture with one eye instead of two, an effort was made to discover if there were not still other ways in which an increased depth illusion might be obtained from a single picture.

A number of other ways were found. Some of these have been described before, others as far as we can discover have not been. Certain of these ways in combination produce a marked depth effect which gives a definite sense of space between the objects represented in the picture and suggest the impression obtained by a stereoscope.

We will first describe the various ways of observing a single picture by which the illusion of depth can be increased. We will in each case also state the most evident modification in our visual functions produced by viewing a picture in the particular way described.

Ways of Increasing the Illusion of Depth From a Single Picture

1. *Looking at a picture with one eye only.* This illusion can be seen by looking at almost any photograph or picture first with one eye and then with two. Strieff[1] who credits Claparade with the discovery describes in detail the increased plasticity and depth which is experienced.

The most obvious effect of using only one eye is the loss of the important factors in depth perception furnished by binocular vision. This loss is very evident if we look with only one eye at actual objects in space. They will appear flatter and with less distance between them.

2. *Looking at a picture through an Iconoscope.* This cannot be described better than has been done by Tscherning.[2] He says, "The iconoscope of Javal resembles somewhat an inverted telestereoscope. . . . The instrument acts as if the eyes were very near each other, at C and C', Fig. 1. Looking at objects through this instru-

[1] Die binokulare Verflachung von Bildern, ein vielseitig bedeutsames Sehproblem. Klinische Monatsblätter für Augenheilkunde, *70*, p. 1, 1923.

[2] Physiologic Optics, Tscherning, Keystone Press, p. 321.

ment the relief disappears: the object appears flat, as in a painting. On the contrary, if we observe an engraving through the instrument, it presents a more pronounced relief than under ordinary circumstances. For, the binocular vision then ceases to make us observe that the different parts of the image are in the same plane, which destroys the illusion. Looking through the iconoscope the relief is more marked than when simply closing one eye."

In this case as in looking with one eye the most obvious effect is the loss of the important factors in depth perception furnished by the parallax of binocular vision.

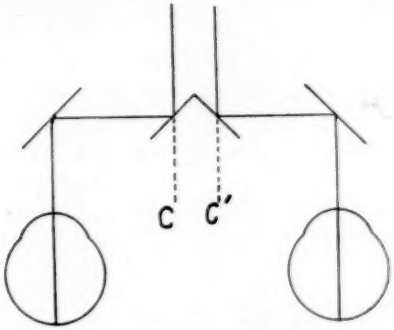

FIG. 1. *The Iconoscope of Javal.*

The increased illusion of depth from an iconoscope over that obtained by simply closing one eye, which Tscherning mentions, is due not to the use of two eyes but to the effect of looking through the instrument. Proof of this is that as much depth is gotten by looking through the iconoscope with one eye as with two. The probable explanation of this will be taken up in describing the increased depth illusion obtained by looking at a picture in a mirror.

3. *Viewing a picture from a greater distance.* A picture gains very considerably in depth by being viewed from a greater distance. This increase in depth can be seen by simply stepping back from a photographic print 8" by 10" or larger after having viewed it from close at hand. It is more marked however in larger pictures seen from greater distances as motion pictures or pictures projected from lantern slides. The most obvious effect of the greater viewing distance is to reduce both binocular and monocular depth discrimination, as their effectiveness falls off rapidly with increase of distance.

4. *Changing the convergence of the eyes from that normally required by the distance from which the piciure is viewed.* This can be done by prisms,

either base in or base out. The more marked illusion is produced by relaxing the convergence. If the picture is held at 50 cm, use 6^{Δ} prisms base in, before both eyes. If at 100 cm, use 3^{Δ} prisms. If the picture is at a distance $\frac{1}{2}$ or 1^{Δ} prisms, which over relax the convergence, increase the illusion. Or better still use the prisms base out. At least one effect of this disturbance of the normal convergence is to upset our judgment of depth. Verhoeff,[3] in the last pages of his article points out the uncertainty in judgment of the size and distance of an object when prisms base out are placed before the eyes. Duane[4] tried the effect of prisms base out upon twenty-eight persons many of them under the influence of mydriatics. In but a single instance was the distant object alleged to be nearer. In twenty-three cases the distant object appeared either smaller or more remote; and in seventeen of the twenty-five cases it was both smaller and more remote; in two cases it appeared smaller but not more remote; in four cases more remote but not smaller. We experienced the same uncertainty of judgment when the prisms were placed base in. Dr. Verhoeff explains the phenomenon as being "dependent upon the disproportion existing between the size of the retinal images of the object and the amount of convergence."

5. *Looking at a picture through a small hole 2 mm or more in diameter held close to the eye.*—This produces an illusion of depth whether used before both eyes or only one, a more marked illusion being obtained if one eye only is used.

The illusion obtained by monocular vision through such a hole is more pronounced than that obtained by monocular vision alone.

The effect is to reduce to a negligible quantity our monocular depth perception dependent upon the aberrations and diffusions of our retinal image.[5]

Though the accommodation is still operative the coordination between it and the diffusion of the image is upset and this upsets the monocular depth judgment. It has been found that if, while looking at an object through a small hole, the accommodation was relaxed and stimulated the object appears to change in size and waver in apparent distance, becoming larger when the accommodation was relaxed and smaller when it was stimulated. The explanation of this phenomenon is probably analagous to that which Dr. Verhoeff gives for a similar

[3] "A Theory of Binocular Perspective, Etc.," Annals of Ophthal; April, 1902.

[4] "The effect of Converging Prisms upon our Notions of Size and Distance." Ophthal. Record *9*, p. 595; 1900.

[5] "Vision and the Technique of Art." Proceedings Amer. Acad. of Arts and Sciences, *58*, No. 1, February 1923.

effect produced by upsetting the convergence. If we look at natural objects through such a diaphram the space between them is reduced and they become flattened.

6. *Changing the accommodation of the eyes from that normally required by the distance from which the picture is viewed.*—This can be done with positive or negative lenses. The more marked illusion for pictures near at hand seems to be produced by relaxing the accommodation.[6] If the picture is at a distance of 50 cm use a plus 2*D* lens; if at 100 cm use a plus 1*D* lens. Using one eye only increases the illusion. If the picture is at a distance negative lenses should be used.

A similar illusion is also produced by using weak cylinders, either positive or negative and with their axis in any meridian.

At least one effect of the use of such lenses would be to upset the coordination between the accommodation and the other depth perception factors and so impair our depth judgment.

If we look at natural objects with such lenses they appear flatter and in reduced perspective. A very complete description of the way in which lenses upset our judgment of perspective is given by MacDougall in "Perspective Illusions from the use of Myopic Glasses."[7]

7. *Looking at a picture binocularly, with one eye receiving a sharp image and the other a blurred one.*—A blurred image can be produced either by a positive or negative lens or cylinder before one eye. The best effect is produced by a plus cylinder with its axis vertical. At normal reading distance a $+3$ to $+4D$ cylinder is good. This blurrs the image in a horizontal direction. When the picture is viewed binocularly this blurring is at least partially suppressed and we see the picture sharp and clearly with a marked illusion of depth much more than we get from one eye alone.

Why we get a greater illusion than with one eye is hard to explain. The fact that a better effect is obtained with a cylinder, which diffuses all vertical lines and leaves the horizontal ones sharp, than with a spher-

[6] Eaton in his article mentions the improved depth effect obtained from a single picture by relaxing the accommodation. He says on page 71 . . . "as we are going to believe ourselves looking at a distant scene our accommodation should be relaxed." From this we infer that he believes the improved depth effect results from putting the eye in the same condition of accommodation as it normally is in when receiving the kind of scene the picture represents. If this is so the depth in a picture of very near objects should not be improved by relaxing the accommodation. We find the contrary to be the case that the depth effect in a picture of object which were but a few inches from the lens of the camera is improved by relaxing the accommodation.

"The Visual Perception of Solid Form" British Journal of Ophthal *3*, pp. 71 and 406; 1919.

[7] Science U. S., *9*, p. 901; 1899.

ical lens which gives a general diffusion suggests that our stereoscopic binocular processes are in some way utilized. Possibly there is a suppression of all parts of the blurred images except that part which with the clear image in the other eye forms a binocular stereoscopic combination in conformity with depth suggestions given us by other faculties.

The effect of blurring the image of one eye is to suppress the depth factors due to binocular vision, as is evidenced by the loss of depth experienced when looking at natural objects.

8. *Looking at the reflection of a picture in a mirror.*—This is a device commonly used by artists to discover defects in drawing and painting.

The effect on our vision is to interfere with our judgment of depth of natural objects in tri-dimensional space as evidenced by the flattening of the perspective of natural objects when looked at by reflection. This loss of perspective is due it is believed to the unaccustomed and indeterminate point of view resulting from looking at a reflection. We

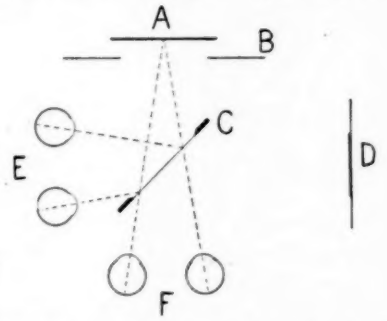

FIG. 2. *Diagram showing multiple framing of a picture.*

are greatly helped in our normal depth judgment by being conscious of the exact relation between our own position in space and that of the objects viewed. This, which is to a large extent given us by our consciousness of all foreground objects and the plane from our feet to the objects in question, is greatly interferred with when we look at a reflection in a mirror due to the framing effect, right and left reversal and the usual accompanying tipping of the field.

The following experiment is quite conclusive evidence that it is our uncertainty as to the exact position of the picture when looking at its reflection that is responsible for the increases in the depth illusion. To make the position of a picture in space as uncertain as possible a half silvered mirror was used as shown in Fig. 2.

A frame *B* was put in front of the Picture *A*. A framed half silvered mirror was placed at *C*. If the picture was viewed with the eyes at *E* its reflection was seen in the half silvered mirror *C*. Light also came to the eyes from the direction of *D*. To cut out this light a black surface on a white background was placed there. The picture was in this way surrounded by three frames. The one at *C* nearest the eyes, the one at *B* a little further away and the one at *D* behind the picture but actually framing it. The total effect was to make one very doubtful as to just where the picture was. The result was an increase in the depth whether the picture was viewed binocularly or monocularly or with the devices above described. It was also found that increased depth was produced if the eyes were put at *F* and the picture was looked at not by reflection but directly. This seemed to prove that depth illusion in looking at a picture in a mirror is not primarily based on the image received being a reflected one but is due to our being made uncertain as to the exact position of the picture in space. The illusion may possibly be enhanced by the luster effect, slight in an ordinary mirror but quite marked in a half silvered one. This same uncertainty of exact relative positions results from looking through any kind of instrument, which limits the field or gives a different point of view, and is believed to be the explanation of why more depth is seen when looking at a picture with one eye through an iconoscope than with one eye without the instrument.

It is probable that the framing of paintings and other pictures is done at least partially for the purpose of causing the observer to be uncertain as to the exact plane of the picture.

The probable reason why looking at the reflection of a picture is helpful to an artist in discovering defects in drawing and modelling will be mentioned later.

9. *Looking at a picture with abnormal rotation of the visual images about the axes of vision.*—This was accomplished by mirrors arranged as shown in Fig. 3. The eyes at *EE'* look through a set of mirrors arranged as shown. By rotating the mirrors *AA* about the axis *aa'* the image coming to the eye *E* is caused to rotate about the axis *EC*. The image coming to the eye *E'* can be caused to rotate in a similar manner about the axis *E'C'* by rotating the mirrors *BB* about the axis *bb'*. The axis *EC* and *E'C'* can be caused to converge on a picture by tipping the two sets of mirrors about the axis *m* and *m'* which are perpendicular to the plane of the paper. If a picture is viewed through this instrument and the image coming to the two eyes are rotated in opposite

directions to almost the limit of fusion the depth illusion is increased. The most evident effect of the above on our normal visual factors is to produce abnormal disassociation of the images on our two retinas and to interfere with our binocular judgment of depth. That our binocular judgment of depth is interfered with is evidenced by the fact that if natural objects are looked at through the mirrors set at the rotations which give the best depth with a picture the perspective is decreased and the objects appear flattened.

A more detailed description of this instrument and some effects produced by it will be given in a later paper.

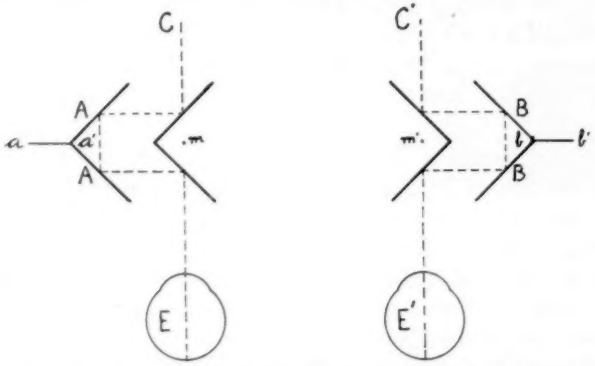

FIG. 3. *Diagram of instrument for rotation of the visual images about the axes of vision.*

SUMMARY

Combinations of certain of the above described means are more effective in producing the illusion of depth than any one of them.

One of the best combinations when looking at a picture near at hand is to relax the accommodation and convergence and use a cylinder before one eye and look at the reflected image of the picture. The depth effect obtained with certain pictures seems to be comparable to that obtained when looking at natural objects, and as stated suggests the illusion obtained with a stereoscope.

Very marked, though not so complete illusion as that obtained with the above combination, is given by using a cylinder before one eye and viewing binocularly. Even monocular vision through a small hole produces quite an illusion.

EXPLANATION OF ILLUSION

Strieff describes at length the explanations which have been given by a number of earlier writers of why greater depth is obtained by monoc-

ular rather than by binocular viewing of pictures. He does not consider any of their explanations satisfactory. He himself considers that the depth seen in a monocularly viewed picture is not paridoxical but is to be expected since we have produced on the eye and brain an exact reproduction of the view represented. He considers that the difficult thing to explain is the lack of plasticity of the binocular impression. This he believes is due to the superposition of the dissimilar impressions received by the right and left eye, a dissimilarity due to the difference in view point and the different impression of vertical and horizontal lines received by the two eyes. This superposition of dissimilar impressions produces a broadening of the picture and a washed out effect of light and shadow resulting in a loss of plasticity and relief. This is accompanied by a tendency of the fixation point to wander over the picture and a general alteration in the relationships in the picture when the fixation is changed.[8]

Tscherning explains the increased depth obtained by viewing a picture through an iconoscope as being due to the suppression of binocular vision which then "ceases to make us observe that the different parts of the image are in the same plane, which destroys the illusion."

It is believed that an analysis of the various ways we have described for producing the illusion of depth and their accompanying effects upon our visual functions will show that the explanation given by Tscherning is not only the proper one for explaining the illusion in that particular case but suggests the basis of the true explanation of the phenomena in all cases, and that that given by Strieff is not adequate.

Before going on to further analysis we will first reconsider the basis of our depth perception.

If we look at a scene in which there are objects at various distances we perceive that some of the objects are nearer and some farther away. This sense of depth results from our ability, due to our knowledge and past experience, to draw correct inferences from certain of the visual sensations and impressions which we receive.

Upon analysis it is evident that we get our impression of depth from these visual impressions and sensations in two quite different ways.

First we get impressions of depth from the reproduction upon our retinas of the characteristics of the viewed objects themselves.

[8] In a paper "Zu der Arbeit von Streiff über die binokulare Verflachung von Beldern" Kl. M.f.A. 1923. Bd *70*, p. 534, Dr. Isakowitz takes exception to some of the explanations offered by Streiff and suggests briefly an explanation similar to ours. Dr. Streiff answers Dr. Isakowitz's criticisms on p. 537, same reference.

Second we get impression of depth from the subjective effects and sensations we experience when viewing the objects.

The first I will call for convenience "Objective Depth Factors," the second "Subjective Depth Factors."

OBJECTIVE DEPTH FACTORS

The following are characteristic of objective depth factors.

(a) Scale or Perspective i.e. relative projected size of objects in the field of view: If we know the size of an object we can judge its distance from its angular size.

(b) Known Forms or Relationships: If we are acquainted with the object at which we are looking or if there is a certain regularity, we easily come to know which part is nearest.

(c) Shadows: Shadows cast by objects are of great assistance in judging their relative distance.

(d) Aerial Perspective: The change of value and color of more distant objects by the veiling effect of the atmosphere is of great assistance in judging the relative distance of the objects.

SUBJECTIVE DEPTH FACTORS

The following are characteristic subjective depth factors.

MONOCULAR

(a) *Accommodation.* Our sense of the muscular condition of the accommodation, or our sense of the muscular change in accommodation actually made or necessary to cause an object to be seen clearly, furnishes us with information as to the distance of the object from our eye.

(b) *Characteristics of the Monocular Visual image.* We get a sense of depth from the fact that every object in space is imaged upon our retina with characteristic diffusions and edges due to its particular position in space relative to the fixation point. This includes the characteristic diffusion both chromatic and achromatic of objects nearer or farther than the focus point and the characteristic radial and tangential accentuation of images on the side of the field of view.[9]

BINOCULAR

(c) *Convergence*: Our sense of the muscular condition of our convergence or our sense of the muscular change in convergence actually made or necessary to cause an object to be seen singly furnishes us with information as to the distance of the object from our eyes.

[9] Op. Cit. "Vision and the Technique of Art."

(d) *Relationship of the corresponding parts of our two dissimilar monocular images, the dissimilarity arising from the different point of view of our two eyes.* This, alone or associated with convergence, is the most important factor for determining the relative position of near objects. It is the factor that is responsible for the effect of depth obtained in a stereoscope.

We will now consider the operation of these two classes of depth factors under different conditions.

When we look at natural objects in tri-dimensional space these two classes of factors supplement each other. For instance if we are looking at two men at different distances the image of the nearer man will be the larger. His image being larger, we infer that he is nearer. This inference will be supplemented by the accommodation and the characteristic monocular diffusion of objects at different distances and the convergence and binocular parallax which will inform us by the difference of position of his images on our two retinas that this man with the large image is in fact nearer.

There are circumstances, however, when the "Objective Depth Factors" and the "Subjective Depth Factors" instead of supplementing, conflict and contradict each other. This is the situation we get when we look at a picture of objects at different distances. For instance suppose we were looking at a photograph taken of the two men at different distances just described. The image of the nearer man is larger than the image of the other and from this we infer that he is nearer. But our binocular stereoscopic vision tells us that the images of both men are at the same distance i.e. on the plane of the picture. This is confirmed by the suggestions we get from our monocular depth perception and our convergence and accommodation, especially if the picture is held near at hand.

With this in mind let us reconsider the effect on our visual factors of the various ways we have described for increasing the depth illusion from a single picture. It will be remembered that in every case the effect of the means used was to interfere with or impair our depth perception due to the "Subjective Depth Factors."

The most marked illusion of depth was obtained where all[10] the factors which contribute to our "Subjective Depth Factors" are suppressed.

The only requisite in all the cases is that the "Objective Depths Factors" should be operative i.e. that is there must be a clear impression of the objective characteristics and relations existing in the scene.

[10] The increased illusion produced by blurring the image of one eye seems to be a supplemental effect.

It seems to be reasonable to conclude therefore that the increased depth effect from a single picture results from removing the conflicting "Subjective Depth Factors" and allowing the "Objective Depth Factors" to carry us their message uncontradicted.

This adequately explains the seeming paradox that an illusion of more depth can be obtained by preventing the functioning of some of our most important depth perception faculties.

Let us return for a moment to Strieff's explanation of the "paradoxe monokulare stereoscope" The fact that the depth obtained by the monocular observation of pictures can be improved upon by the various ways that have been described, seems to refute his assumption that a complete depth effect follows naturally from monocular observation.

His belief that the lack of plasticity and depth which accompanies binocular observation of pictures is due to the superposition of the dissimilar impressions received by the right and left eye is difficult to accept in view of the fact that a most marked illusion of depth can be obtained where a cylinder is used in binocular observation of a picture.

As we have seen, in a single picture "Subjective Depth Factors" can largely negative the "Objective Depth Factors." In a stereoscope we cause the "Subjective Depth Factor" of binocular parallax to supplement instead of contradict the "Objective Depth Factors." Under certain conditions, however, the "Objective Depth Factors" can overcome at least the most important of our "Subjective Depth Factors." An example of this is the refusal of a pseudoscope picture to reverse if there is a marked objective perspective in the scene.

There is one "Subjective Depth Factor" which can be made use of in increasing the depth illusion in a single picture. That is the monocular depth perception due to the aberrations and diffusions of the retinal image. These characteristics of the images can be reproduced in a picture as described in "Vision and The Technique of Art"[11] and increase the illusion of depth.

As to the question why looking at a reflection helps a painter see defects in the modelling and drawing of his painting, it is found that these defects become still more marked if all the "Subjective Depth Effects" are nullified. The explanation offered is that when we are relieved of all but our "Objective Depth Factors," 1st, we are freed of a confusion, which allows us to see more truly, 2nd we are then relying solely upon relative size, perspective, form and shading for an

[11] Op. Cit.

illusion of depth and any discrepencies or defects in the representation of these factors becomes very apparent.

We would suggest for the use of artists for the above purpose, as an improvement over a mirror, a pair of glasses of the proper prisms, lenses and cylinder for the distance required, or if something more simple is wanted a cylinder before one eye viewing the picture with both eyes. A $+2.5D$ cylinder with axis vertical is good for intermediate viewing distances. Its strength can be varied by moving it nearer or farther from the eye.

The following interesting points relative to depth perception of objects in tri-dimensional space are brought to mind by the facts presented.

First. The factors which contribute to our depth perception consist of two clearly differentiated groups as above described under the headings of "Objective Depth Factors" and "Subjective Depth Factors."

Second. In the perception of depth in tri-dimensional space the following "Subjective Depth Factors" play a part.

(a) Character of the monocular image.
(b) Corresponding images on both retinas.
(c) Rotation of the visual fields about the axis of vision.
(d) Convergance.
(e) Accommodation.

Third. The direction and distance of the viewed objects require a particular adjustment of each of these factors.

Fourth. If the adjustment of any one of these factors is disturbed there is an impairment of the depth perception.

Fifth. It would be of interest to determine whether the best depth perception is only possible with the ideal adjustment of these various factors or whether starting with any adjustment it can be developed with visual experience.

Sixth. If the former is the case it is suggested that the inter-relation of the adjustment of these various factors should not only be considered by ophthalmologists in prescribing correcting glasses but that depth perception may be a key as to whether or not a proper relationship between various visual functions has been obtained.

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INSTRUMENT SECTION

A NEW NON-INTERMITTENT SENSITOMETER

By Arthur C. Hardy

ABSTRACT

A new non-intermittent sensitometer has been constructed which consists of two sector wheels rotating about the same axis at different angular speeds. During the exposure, the larger disk makes only one revolution. In this interval, the small disk makes many revolutions but the large wheel covers the photographic material except for one revolution of the small wheel.

With the ordinary sector wheel sensitometer, the exposure range is rarely more than 256 to 1 because of the difficulty of cutting the wheel. It is shown that by using two sector wheels, the exposure range may easily be increased to 16,384 to 1. An extension of this principle to three disks would not involve any serious mechanical difficulties and would increase the exposure range to more than one million to one.

Photographic research generally requires an instrument of some sort, called a sensitometer, to expose the photographic material to radiation of known intensity and quality for known periods of time. Because of the well known intermittency effect,[1] the exposures received by the photographic material should be continuous (non-intermittent).

Two types of non-intermittent sensitometers have been described recently by Jones. In one,[2] the duration of exposure is governed by means of a magnetically operated plate in front of the photographic material. This plate moves, one step at a time, at intervals determined by slots cut in a long length of motion picture film. The film is driven at constant speed and an electrical circuit is completed as each slot reaches a contact maker. Although this type of sensitometer allows changes in the exposure to be made very easily by using a new piece of film with differently spaced slots, it is somewhat unsatisfactory for general purposes because of the time required to make an exposure. It is impossible to obtain sufficient precision when the shortest time interval is less than 0.5 second. If the light intensity is adjusted to give a just perceptible deposit on a high speed material for this exposure, it is necessary to have some exposures as long as fifteen or twenty minutes when testing materials of lower sensitivity. Not only is it inconvenient to maintain the light intensity constant over so long a period, but, due

[1] Abney, W. de W: Phot. Jour. *18*, p. 56; 1893.

[2] Jones, L. A: Frank. Inst. J. *189*, pp. 303-329; March, 1920.

to the failure of the reciprocity law,[3] the results obtained are not strictly applicable to general practice where the exposures are usually much shorter.

The second type of non-intermittent sensitometer described by Jones[4] consists of the usual form of sector wheel, but arranged to make only one revolution during the exposure of the photographic material. This type of sensitometer is free from the error due to the intermittency effect but is still open to the objection that the total exposure-range is limited by the difficulty in cutting more than about nine power-of-two steps in a wheel of ordinary size. Suppose, for example, that the largest sector comprises 180°. The angle subtended by the ninth sector will then be $180/2^8$ or 0.7°. Assuming that the error in cutting the smallest sector is only 0.001 inch, the sector wheel must be at least sixteen inches in diameter if an accuracy of 1% is desired in the exposure. Nine power-of-two steps are usually sufficient to cover the useful exposure-range of the average photographic material, but they provide no margin for variations in sensitivity of different emulsions. The exposure required to reach the shoulder of the characteristic curve of a slow plate is approximately five thousand times the exposure required to give a just perceptible deposit on a very fast plate. Thus, a sector wheel having at least thirteen steps is desirable but is manifestly impracticable in the usual form. It is possible, although not at all desirable, to increase the exposure range by changing either the period of revolution of the sector wheel or the intensity of the source of light. It occurred to the author that the same purpose might be accomplished by using two sector wheels rotating at different speeds about the same axis and in approximately the same plane.

Fig. 1 represents two such wheels comprising a fifteen step sensitometer. The large disk is of the usual type and bears nine power-of-two steps. The six shortest exposures are accomplished by the small disk which rotates faster than the large disk. Thus the small disk turns through a larger angle in a given time and it is therefore possible to cut sectors on the small disk which could not be cut on the other. The aperture *ABCD* in the large disk is so designed that the photographic material is exposed during a single revolution of the smaller disk. In this way the intermittency effect error is avoided and the exposure-range of the ordinary sector wheel is enormously extended.

[3] Schwarzschild, K: Phot. Corr. p. 171; 1899.
[4] Jones, L. A.: J.O.S.A. & R.S.I., 7, pp. 305-309; April, 1923.

DESIGN OF SECTOR WHEELS

The salient features of the design of the sector wheels will be most readily understood if they are assumed to be already constructed and in rotation. The operation of the large wheel is then obvious. Starting from a position such as is shown in Fig. 1, it makes one complete revolution and stops. This registers the nine longest exposures as the region between F and E sweeps across the plate. Now, suppose that the small wheel is geared to rotate at K times the angular velocity of the large wheel. Let us suppose further that the small disk is so placed on its shaft that the point T of the small disk and the line AB of the large

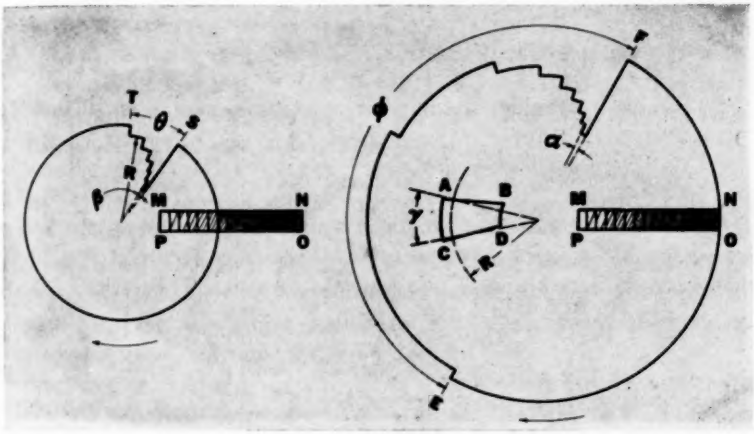

FIG. 1. *Drawing of the two sector wheels which rotate about the same axis but which are shown with their axes of rotation separated for the sake of simplicity. The position of the photographic material with respect to each wheel is indicated by the rectangle MNOP. The source of light lies behind the plane of the drawing on the perpendicular erected at the center of the rectangle.*

disk reach the upper edge of the plate MN together. Until this time, the portion of the plate lying behind the small wheel has been protected by the large one. As AB crosses MN, the opening in the large disk begins to uncover the last six steps of the plate so that as S arrives at MN, the exposure of these steps will start. Obviously, AB must reach PO before S does, in order that the entire width of the plate may be exposed. The longest exposure controlled by the small wheel will end as T reaches PO. It is evident that CD must not arrive at MN before T. The size of the aperture $ABCD$ must be so chosen that the edge CD will arrive at PO before S arrives there for the second time.

If these conditions are all fulfilled, the aperture in the large wheel will allow the small wheel to expose the photographic material during only one revolution.

Let us first design the large wheel. Assume that the largest sector in the large disk is 180° ($\phi=\pi$ radians). This simplifies the cutting of the wheel and also allows ample time for it to arrive at a constant angular velocity before the exposure starts. Let α represent the smallest sector on the large disk. If n is the number of power-of-two steps on the large disk,

$$\frac{\phi}{\alpha}=2^{n-1} \tag{1}$$

or, solving for n,

$$n=\frac{\log(2\phi/\alpha)}{\log 2} \tag{2}$$

By similar reasoning, the number of steps m on the small disk is

$$m=\frac{\log(2\theta/\beta)}{\log 2} \tag{3}$$

Obviously, the exposure produced by the small sector of the large wheel should be twice that produced by the large sector of the small wheel, assuming a power-of-two scale throughout. This requires that

$$\theta=\frac{K\alpha}{2} \tag{4}$$

Substituting the value of θ from equation 4 into equation 3 and adding equations 2 and 3, we obtain an expression for the maximum number of power-of-two steps that are possible.

$$m+n=\frac{\log(2K\phi/\beta)}{\log 2} \tag{5}$$

It is interesting to note that this depends only on the gear ratio K and the angular size of the smallest sector that we chose to cut in the small disk, α having been eliminated from the expression.

We have thus far overlooked the fact that, during the time that the small disk is turning from the position where T is at MN to the position where S is at PO, the edge of the aperture in the large disk must have turned from MN to PO. This is expressed by the following relation where W is the width of the plate MP.

$$\frac{W}{R}=\frac{2\pi-\theta}{\lfloor K\rfloor}+\frac{W}{\lfloor RK} \tag{6}$$

or, solving for W,

$$W=(2\pi-\theta)\frac{R}{K-1} \tag{7}$$

A similar expression would result, were we to consider the fact that the edge CD must cross the plate while the small disk turns from the position where T is at MN to the position with S at PO. If we substitute the value of θ from equation 4, we obtain

$$W=\left(2\pi-\frac{K\alpha}{2}\right)\frac{R}{K-1} \tag{8}$$

The width of the plate actually used may be smaller than W but it must not exceed the value indicated by equation 8.

The angle subtended by the aperture $AECD$ at a distance R from the center can be obtained by considering the fact that AB and S arrive at PO together and that subsequently CD and T arrive at MN together. This leads to the expression,

$$\gamma=\frac{W}{R}+\frac{\theta}{K}-\frac{W}{RK} \tag{9}$$

These equations suffice to design a pair of sector wheels to suit any set of conditions which are not mutually contradictory. Probably the most satisfactory method of illustrating the successive steps in the process is to work a numerical example.

Assume that it is desired to build a non-intermittent sensitometer with an exposure range of 2^{14}. This means that the total number of steps will be 15. Let us further assume that the radius R is to be six inches. (This can be altered later if it is found necessary.) With a wheel of this size there is no particular difficulty in cutting the sector β as small as $\pi/2^8$ radians. Substituting in equation 5, we find $K=64$.

We next substitute in equation 8 to make sure that the plate will be of sufficient width to be useful. Since it is advantageous to have W as large as possible, α should be as small as possible. Assume α equal to β. (Actually α might be slightly smaller). Making this substitution and solving equation 8, we find that W equals 0.56 inches. Since only nine milimeters of width are required to measure densities with such an instrument as the Martens photometer, W is evidently large enough to allow some overlap, which is desirable.

Substituting in equation 2, we find that there must be nine steps on the large wheel. Equation 4 indicates that the largest angle on the small disk is $\pi/8$. Substituting this in equation 3, we find that there

must be six steps on the small disk which makes the total of fifteen steps. The various sectors will then be cut as follows

Large Disk		Small Disk	
Step 1	180°	Step 10	22.5°
2	90	11	11.25
3	45	12	5.625
4	22.5	13	2.812
5	11.25	14	1.405
6	5.625	15	0.703
7	2.812		
8	1.405		
9	0.703		

The angular size of the aperture in the large disk $ABCD$ is found from equation 9. Substituting the values previously found for the various quantities, γ is equal to 0.0979 radians or 5.6°. This is the angle between AB and CD at a distance R from the center of the wheel. Since the six shortest exposures start simultaneously, the edge AB should be cut so that it will coincide with PO when the large wheel is turned to the proper position. The shape of the edge CD can be obtained by substituting in equation 9 the successive corresponding values of R and θ. The aperture $ABCD$ may be placed at any point between E and F and the relative position of the two disks on their shafts may subsequently be adjusted to correspond.

CONSTRUCTIONAL DETAILS

An instrument designed according to the principles just outlined has been constructed and is in operation in the photographic laboratory. This model, shown in Fig. 2, has 13 power-of-two steps.

The disks were cut from 1/16 inch sheets of aluminum in the manner described by Sheppard and Mees.[5] The accuracy in cutting was sufficient to insure an exposure error less than 1% in any step. An alternating current motor operating at 1800 R.P.M. ($\pm 1\%$) drives the small disk through a single thread, 30 tooth, worm and worm wheel. In consequence, the small disk makes one complete revolution each second. The large disk runs freely on the shaft carrying the small one and is driven by back gears in much the same manner as the minute and hour hands of a clock mechanism. The gear ratio in this case was 32 to 1, produced by two pairs of 20 pitch gears with ratios of 160/20 and 144/36. Although this pitch is coarser than is required by the load imposed, gears of this diameter reduce the angular back-lash to a point where it has a negligible effect on the time of exposure.

[5] Sheppard and Mees: "Investigations on the Theory of the Photographic Process" (Longmans, Green and Co. 1907).

A photograph of the assembled apparatus is shown in figure 3. The source of light is a 21 candle-power, 6 volt automobile headlight lamp, operated from an independent storage battery, a potentiometer being

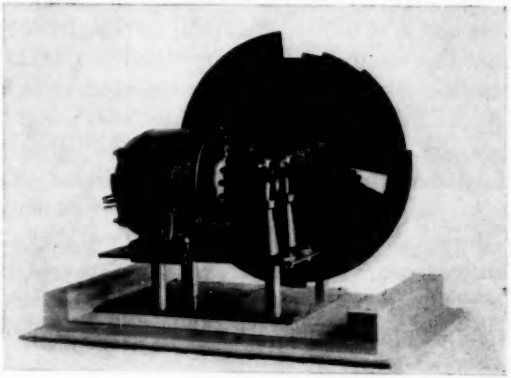

FIG. 2. *Photograph of the shutter mechanism of the sensitometer. In this model, the large sector wheel contains five steps and the small sector wheel eight steps. The motor drives the small wheel at the rate of one revolution per second by means of the worm gear. The large wheel is driven by the small one through a train of back gears which does not show in the photograph. The period of revolution of the large wheel is thirty-two seconds.*

used to indicate the potential difference between wires soldered to the contacts on the base of the lamp. The lamp is operated at a color

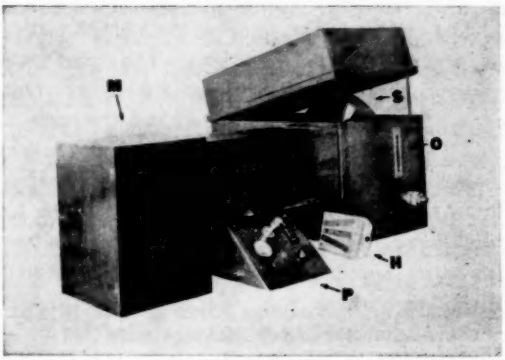

FIG. 3. *Photograph of the completed sensitometer showing the lamp house (M), the potentiometer (P), the sector wheels (S), the plate holder (H), and the plate holder slot (O). The lamp house is readily detachable so that other sources of light may be used at will.*

temperature of 2360 K. and is screened to approximately daylight quality by means of a Wratten No. 79 filter. The distance from the

light source to the plate is one meter. A hole is provided at the end of the box behind the photographic material to allow the illumination falling on the plate to be measured with a portable photometer.

The size of the plate used is $5 \times \frac{3}{4}$ inches, there being thirteen steps 3/8 inches long and 9/16 inches wide. Since a complete cycle of events is repeated by the rotating disks every $360/K-1$ or 11.60 degrees, there is the theoretical possibility of exposing as many as fifteen plates at each revolution of the large disk, provided they are placed radially 11.60 degrees apart. Actually, this would require that the light source be at a greater distance from the plate than is desirable. With the light source one meter away, it was found possible to expose three sensitometric strips during each revolution of the large wheel, the illumination being sufficiently constant over this area. The plate holders were made to hold three plates in their proper respective positions when fully inserted in the plate holder slot. It was often found desirable to use plates or films which were only $4\frac{1}{4}$ inches in length instead of 5 inches. This permits only eleven steps out of the thirteen to be used and different plate holders have been constructed to allow the eleven steps to be selected to suit the sensitivity of the photographic material being tested. In testing a low-speed material, the plate is moved toward the periphery of the disks and in the opposite direction for a high-speed material.

In order that the large wheel might make one revolution and stop automatically, a two segment commutator is used with a double-throw snap switch. The circuit is the same as that employed to control an electric circuit from either of two locations. The commutator is rotated at half the speed of the large disk by a chain drive. Thus, when the switch is snapped, the circuit is completed and the large disk revolves one revolution. The commutator then automatically breaks the circuit and the disk remains at rest until the switch is again snapped, connecting the power to the other commutator segment. The time required for the large disk to come to constant speed is less than one second and the time required in stopping is six seconds. This is well within the half period of the large wheel.

In closing, the author wishes to acknowledge his indebtedness to Mr. L. E. Clark and Mr. S. Kirshen for their assistance in the design of this instrument and to Mr. Carl Selig and Mr John Rosen for their painstaking care in the construction of it.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASS.
SEPTEMBER 19, 1924.

PRECISION DENSITOMETERS FOR PHOTOGRAPHIC PHOTOMETRY

By George R. Harrison[1]

ABSTRACT

After discussion of the advantages of physical densitometers and microphotometers over the older types using the eye method, the merits and disadvantages of the more important recent designs are summarized. The conclusion is reached that the thermoelectric densitometer is most accurate for direct-reading work, while the photoelectric cell is best adapted for the null method. The disadvantages of the thalofide cell and the selenium cell seem to outweigh their only advantage of large currents.

A simplified standard type of direct-reading densitometer is described, with vertical optical system, in which accuracy equal to the best claimed for the photoelectric null method, one-tenth of one per cent, was attained. The sensitivity was such that 1000 mm deflections on an easily read scale were obtained through a clear plate with a slit .05 mm wide, using only 20 watts in a lamp rated at over 70 watts. A single easily constructed thermocouple was used with a low resistance d'Arsonval galvanometer. Curves are given showing the gradual improvement of deflection steadiness, from variations of two per cent to almost complete steadiness, as various sources of disturbance were eliminated.

With the growing importance of photographic photometry in the past few years numerous descriptions have appeared of instruments designed to measure the density of any part of a photographic plate. The older form of photometer in which the eye compared the transmission of the deposit to that of a standard wedge has gradually given way to the physical microphotometer or densitometer, this being simpler in construction, easier to operate, and in general giving more reliable results. So many forms of densitometer have recently appeared that a person studying the field for the first time is apt to have difficulty in determining which type will be best for his particular work. The purpose of the present paper is to summarize the advantages and disadvantages of the more important physical densitometers. The most convenient for ordinary use is an instrument which will give the ratio of the light transmitted by a plate to that incident on it with negligible error, quickly, and with the least effort. Since the accuracy of photographic-photometric methods depends upon being able to make a large number of determinations of the same quantity, the element of time is very important.

Four principal types of physical densitometer may be distinguished, using the thermoelement, the photoelectric cell, the thalofide cell, and the selenium cell as measuring agent, respectively. Each of these can

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be made to function more or less satisfactorily, but they are by no means comparable in results.

The optical systems used in most physical densitometers differ only in minor details. In the direct-reading type light from a constant source is focused by a condenser on a slit, and an image of this is thrown on the plate to be measured. An image of the illuminated portion of the plate is in turn thrown on the receiving element, and from its response with plate interposed and removed the ratio of transmitted to incident light can be obtained, after certain corrections have been made. There are various simplifications and modifications of this system, which do not however, change its general features. In the null method light passing through the plate to be measured is balanced against that through a standard wedge which has been previously calibrated.

Thermoelectric Densitometers. Stetson[2] describes a thermoelectric photometer, designed primarily for measuring stellar images, but useful also on spectrum plates, using a Coblentz surface thermopile as receiving element. The optical system allowed focusing on the thermopile visually, and the direct deflection method gave compactness and convenience. He used a vertical optical system, the light being above the table carrying the plate to be measured, and the thermopile being below. Stetson and Carpenter[3] have recently described improvements in the instrument, and a series of tests on plates that were run with it.

Moll,[4] having designed a new type of quick-acting thermopile and a short period galvanometer, applied them to a densitometer of the direct reading type, and describes an instrument which responds in less than three seconds, with a horizontal optical system. Pettit and Nicholson[5] improved the original Koch[6] microphotometer by substituting a thermopile for the photo-electric cell. They arranged a system of parallel mirrors in their thermopile tube so as to increase the length of line available in measuring a spectrum plate, and could use either sunlight or light from a high power lamp to illuminate the slit. They used a vacuum thermopile of Bi/Bi-Sn alloy, and a d'Arsonval galvanometer.

Siegbahn[6] has recently described a thermoelectric densitometer which worked very satisfactorily in measuring x-ray plates. He concentrated a very small image of the light source on the plate, and enlarged this so that it covered the whole of a linear thermopile 15 mm long. He had

[2] Stetson, Astrophysical Journal, *43*, pp. 253 and 325; 1916.
[3] Stetson and Carpenter, Astrophysical Journal, *58*, p. 36; 1923.
[4] Moll, Phys. Soc. Lond. Proc., *33*, p. 207; 1921.
[5] Pettit and Nicholson, J.O.S.A. & R.S.I., *7*, p. 187; 1923.
[6] Siegbahn, Phil. Mag., *48*, p. 217; 1924.

some trouble with graininess of the plate being measured. The writer[7] designed a densitometer with a horizontal optical system, using a radiomicrometer as receiving element. This had the advantage of being as sensitive as a thermopile with Thomson galvanometer yet with the steadiness of a d'Arsonval, and was very satisfactory.

The characteristics of the thermoelectric type may be summed up as: 1 Quick action, periods down to three seconds being possible of attainment. 2. Direct reading, the deflections being closely proportional to light intensities; the plate can therefore be moved across the slit, and automatic registration of the galvanometer deflections will give an opacity curve for the plate being measured. 3. Permanence, since the thermopile is not easily injured by light of too great intensity, nor can it be harmed by light of the wrong color. Once the receiving element is installed it is by no means fragile if properly constructed, and if not of the vacuum type requires little further attention.

Photoelectric Densitometers. The original physical microphotometer of the modern type was designed by Koch,[8] using a photoelectric cell. He showed the advantages of this type over the eye method, his instrument being direct reading and fitted for automatic registration. When Pettit and Nicholson substituted the thermopile for the cell, however, the results were greatly improved, and further data seem to indicate that the thermoelectric receiver is the best type for direct reading densitometers.

Dobson[9] uses the photoelectric cell in a null method, it being exposed alternately to a beam through the plate being measured and to another through the standard wedge. With this method he attains an accuracy of one-tenth of one per cent, which is the highest claimed for any photometer and leaves nothing to be desired in the way of precision. It has the one drawback of all null methods, however, in that two operations, balancing and reading the wedge, are required, where one suffices in the direct-reading method. Also it does not lend itself readily to automatic registration. Behr[10] has designed an improvement on this method, whereby the galvanometer connections are reversed as the exposure is changed, and the resulting deflection balanced by a counter emf. Apparently this can be made to serve for automatic registration, but the apparatus required is more complex than in any thermoelectric type.

[7] Harrison, J.O.S.A. & R.S.I., *7*, p. 999; 1923.
[8] Koch, Ann. der Phys., *39*, p. 705; 1912.
[9] Dobson, Proc. Roy. Soc., *104*, p. 248; 1923.
[10] Behr, Boston meeting Opt. Soc. Am., Oct. 1924.

The null method is, however, an answer to the objection that the sensitivity of the photoelectric cell varies with age, color of light stimulus, and impressed voltage.

Gibson[11] has used the photoelectric cell in transmissometry, where the requirements are very similar to those of densitometry. He developed a satisfactory null method, and also a direct method based on it, with the same sort of complexities referred to above. He found that a method which was satisfactory with one set of photoelectric cells had to be modified when new ones were substituted for them.[12] Perrine[13] mounted a photoelectric cell on a comparator carriage, using a 100 watt lamp and a slit .25 mm wide. He had some difficulty with dark currents.

The advantages of the photoelectric cell for densitometry are quickness of response, high sensitivity, and insensibility to scattered heat rays. Its disadvantages are its variation of sensitivity with numerous factors, its variable response to light of different colors, leakage currents, fragility, and limited life. It cannot be considered as satisfactory for a simple direct-reading method, but gives the highest accuracy in a null method, and with certain additional features can be used for accurate direct-reading work.

Selenium and Thalofide Cell Densitometers. Toy and Rawling[14] substituted a selenium cell for the photoelectric cell in using Dobson's method. The advantages they claim are a larger current, more compactness, and convenience. Dobson criticizes their use of the selenium cell on account of its large lag, and his method apparently gives both greater accuracy and quicker results. Schoen[15] found that a thalofide cell could be used to measure very low densities particularly well, especially those too low for visual photometers. This advantage of course applies to all of the physical photometers discussed. He could not use any but the red or infra-red in measuring a plate, since blue produced a permanent change in the cell. There was a dark current which had to be annulled, but this was possible when the null method was used. The sensitivity of the cell varied with the voltage, however, and there was a large lag.

Bazzoni, Duncan, and Mathews[16] describe a densitometer using a thalofide cell in which they used the ballistic method. The voltage had

[11] Gibson, J.O.S.A., *2*, *3*, p. 23; 1919.
[12] Gibson, J.O.S.A. & R.S.I., *7*, p. 693; 1923.
[13] Perrine, J.O.S.A. & R.S.I., *8*, p. 381; 1924.
[14] Toy, Proc. Phys. Soc. Lond., *36*, p. 432; 1924. (See also Price, letter to Nature, p. 351, Mar. 8, 1924.) Toy and Rawling, J.S.I., *1*, p. 362; 1924.
[15] Schoen, J.O.S.A. & R.S.I., *7*, p. 483; 1923.
[16] Bazzoni, Duncan and Mathews, J.O.S.A. & R.S.I., *8*, p. 381; 1924.

to be applied to the cell one or two hours before starting, however, and a constant temperature was found necessary. These workers enlarged their plates before measuring them in order to use a wider slit, which of course introduces new errors.

The advantage of large currents obtained with the selenium and thalofide cells seems to be completely offset by their slowness of response, change in sensitivity with temperature, impressed voltage and life, and their delicacy. Although they can be made to serve as measuring devices in physical densitometers they seem to be neither as convenient nor as accurate as either the photoelectric cell or the thermopile. A comparison of the various types therefore leads one to the conclusion that the thermoelectric type is most satisfactory for direct-reading work, and the photoelectric type, on account of its greater sensitivity and quicker response, for the null method. The latter advantage is largely over-balanced by the increased number of operations required in the null method, this increasing the time for each reading, so improved sensitivity seems to be the only thing in its favor coupled with the fact that an accuracy of one-tenth of one per cent has never hitherto been attained with a direct-reading instrument. The purpose of the work to be described in the balance of this paper was to see whether such an instrument could be made to reach this degree of precision.

Photographic plates vary so in sensitivity over their surfaces that similar points cannot be expected to agree to within more than two or three per cent, but by averaging many values accuracy to within one per cent is possible. There is therefore no need that the average densitometer be more accurate than one-fourth of one per cent, and it would seem unwise to sacrifice either sensitivity or speed for greater precision.

We may list the following desirable specifications for a densitometer as used in ordinary photographic photometry.

1. Direct reading.
2. Sensitive, so that deflections of 1000 mm on an easily read scale can be obtained through clear glass with a slit width of .05 mm.
3. Quick acting, response to take no longer than six seconds, this being the average time required for recording the previous result.
4. Stable, so that the zero can be counted on to not vary more than three mm in sufficient time to make ten deflections.
5. Permanent, so that its sensitivity does not vary with age or conditions of temperature, illumination, or mild abuse.
6. Accurate to a few tenths of one per cent.
7. Deflections proportional to light intensities.
8. Dead beat, so that ballistic or steady deflections can be used.
9. Cheap and easily constructed.

These specifications are completely fulfilled by the instruments to be described. By combining various features of the thermoelectric densitometers listed above, and making a careful search for the sources of error in two working models, it has been found possible to meet all these conditions without introducing any complexities of apparatus; in fact, the desired end was reached by simplification. No limit to the accuracy obtainable was found, but as used in daily work the errors introduced by the apparatus are negligible, being about one-tenth those due to errors from other causes.

To minimize fragility and for ease of construction, a single thermocouple was used as receiving element. This was made of bismuth and silver according to the method of Coblentz, and since the little skill required in making such a couple is possessed by the average experimenter, and the materials are readily procurable, the problem of obtaining the sensitive receiver is not great. Thermopiles are much more difficult to construct, but a single couple was found entirely sensitive enough with the galvanometer and optical system used.

The thermoelement, shown in Fig. 1, *a*, is constructed of bismuth wire .1 mm in diameter, and silver wire .05 mm in diameter, with blackened tinfoil receiver and radiator. These were 1.5 mm long and .25 mm wide, which was the approximate size of the image of the slit thrown upon the hot junction. They were made as small as possible to reduce lag. The manner of mounting on a wooden holder with sealing wax is shown in Fig. 1, *b*, showing also the optical system finally adopted. This simple form was chosen as giving high light intensity, and the slit widths available with it were quite satisfactory. The vertical optical system was chosen, since this enables the plate to be laid flat on a table, emulsion side down, on a sheet of paper with a hole over the slit, and it can be quickly placed in the proper position for measuring. Since the slit is necessarily an appreciable distance from the emulsion side of the plate being measured, the equivalent width of the slit is greater than its actual width, due to the spreading of the light beam. The separation was made a minimum by having the slit housing adjustable in vertical ways; after the plate is in place, the slit is brought up to it as closely as possible without actual contact. The surfaces of the slit jaws were made slightly convex, so that they could even touch the emulsion without scratching when moved. In general true slit width and equivalent width did not differ by more than fifty per cent. This also compensates for the fact that practically all plates are concave on the emulsion side, since in measuring spectrum lines a change in equivalent slit width may

introduce serious errors. The arrangement is similar to Stetson's, except that here the light is placed below and the thermo-couple above, whereas he had the light above and the thermopile below. Two densitometers of the type shown in Fig. 1 are in use, one being a "spotting" instrument where a given portion of the plate can be laid over the slit and its density measured, and the other a "running" type, where a

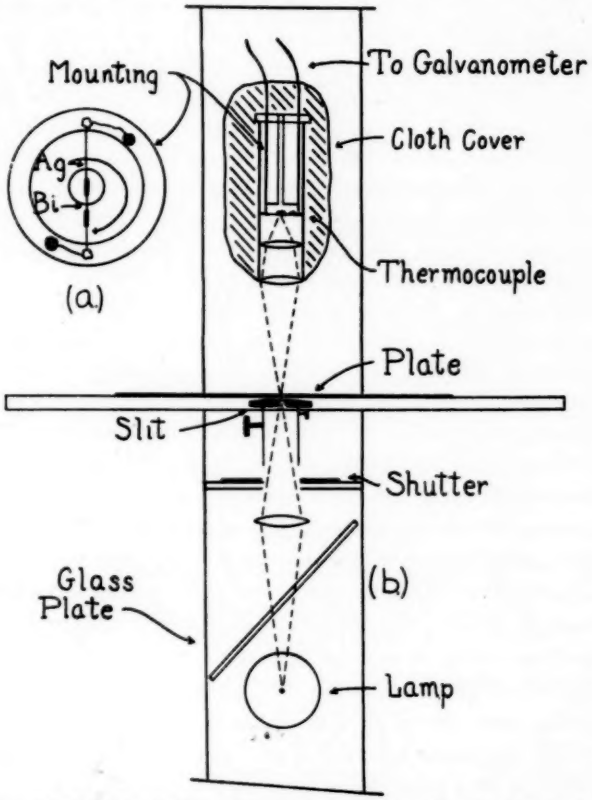

FIG. 1. (a) *The bismuth-silver thermocouple mounted on the end of its wooden cylinder.* (b) *Diagram of the final simplified densitometer for precision to one-tenth of one per cent.*

carriage is provided with a screw drive run by a synchronous motor, which moves the plate at a uniform speed across the slit.

The galvanometers used are Leeds and Northrup d'Arsonval types, one having 12 ohms resistance and a period of six seconds, sensitivity 14.1 mm per microvolt, and the other 20 ohms resistance and one-third

that sensitivity. Sufficient resistance is put in series with each thermocouple to make the galvanometer just dead-beat, though if higher sensitivity were desired this could be cut out, making the period slightly longer.

Several types of lamp have been used, but those finally settled on were street-lighting straight helical filament tungsten lamps, drawing 6.6 amps at 10-12 volts. These have a large bulb, which decreases the rate of blackening, and when run on six volts they have a practically endless life. This also runs them on a flatter part of the current-emission curve, so that a given change in battery voltage produces a smaller change in total energy emitted. It was found that sufficient sensitivity was attainable to use them at this low brilliancy for practically all work, but for very high densities they could be run at full voltage, giving over five times the light intensity. The lenses were taken from old Navy sighting telescopes, and were uncorrected. A shutter was provided to take null readings at occasional intervals.

No difficulty was found in getting deflections of 1000 mm on an easily read scale at 2.5 meters; in fact, for the spotting densitometer the light intensity is such that for a normal slit width of about .1 mm the deflection through a clear emulsion on glass is 1800 mm on a scale at 3.5 meters, which is easily read with a magnification of 20. The instruments are dead beat, respond within six seconds, and are not easily thrown out of adjustment, the various parts being very rigidly mounted. The galvanometer telescope was placed on a level with the eye when the observer is seated in front of the table carrying the plate to be measured. It was found at first that the zero was unsteady, and that at a deflection of 1000 mm the reading varied from 10 to 20 mm continuously, so that accuracy of more than two per cent could not be expected. In Fig. 2, *a* shows this condition, as registered on a strip of sensitive paper wound on a rotating drum driven by a synchronous motor. The total length of the record represents a period of 12.5 minutes, the deflection being about 1000 mm on a scale at the same distance as the drum.

The probable sources of unsteadiness were then traced and found to be:

1. Variable voltage in battery which fed lamp.
2. Variable voltage from loose contacts in lamp line.
3. Air currents on thermocouple.
4. Stray light varying in intensity.
5. Varying slit width, due to air currents.
6. Dust particles getting into slit.
7. Varying water vapor or CO_2 in air.

8. Mechanical displacement and vibration in apparatus.
9. Thermal agitation of thermocouple due to expansion and contraction.
10. Changing refractive index of air in slit due to convection currents from lamp.

Each possible source of error was traced; all connections in the lamp feeding circuit were soldered, except the battery contacts, which were made with tightly clamped spikes sticking into the lead. A new storage battery was used; the thermo-couple was covered more closely, and finally a piece of plate glass was placed at 45° above the lamp and shutter to turn convection currents to one side. The elimination of these air currents caused the most marked improvement, since they caused variable amounts of light to get through the comparatively small aperture of the slit. Each of the changes made improved the

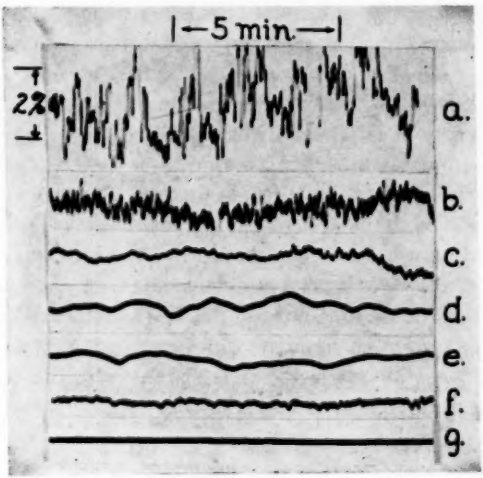

FIG. 2. *Densitometer tracings showing the gradual progress made in eliminating sources of unsteady deflection.*

steadiness of deflection somewhat, and the successive tracings of Fig. 2 show the gradual elimination of variations as the various sources of error were removed. All these records, with the exception of *g*, were taken for steady deflections of 1000 mm at the same distance from the galvanometer, and it is evident that the improvement goes from variations of two per cent in *a* to two-tenths per cent in *f*. *g* shows the curve given by the densitometer as finally used, the drum not being the full 2.5 meters from the mirror as in the others; curves as smooth as *g* could be taken at that distance, however, as is evidenced by a comparison of *e* and *f*. In *e* the short period errors have all been re-

moved, leaving only those of from one to five minutes; in *f* the long period errors are missing but the short period ones have been re-introduced. The changes required in eliminating these errors also eliminated all zero drift for steady readings, with the exception of a steady drift at the beginning as the instrument is warming up, and a slow long period variation of several millimeters. The first is eliminated by turning the light on ten minutes before beginning readings, and the second by having the telescope slightly movable about a vertical axis, so that every ten readings it can be reset on the zero. In this way all other zero corrections are eliminated. The absence of other zero drift may be explained by ascribing it to the removal of all slits or windows near the thermo-couple; it is protected from air currents by the lens several inches below it, and by its thick housing. It requires no slit, since all unintercepted energy goes by and is absorbed by the walls.

The running densitometer, where the highest accuracy is desired, is kept in a dark room of its own; the spotting densitometer, however, is kept in the corner of a laboratory where one may be confident of measuring a plate to .5 of 1% with it on ten minutes notice at any time, with no particular need of taking precautions for accuracy. The test for steadiness as made above is of course not a complete test for absence of error. Accordingly a series of reproducibility tests was run, with no attempt made to create special conditions. After the spotting densitometer had been in use for some months it was subjected to the following tests in a large open room in which other work was in progress. The readings were all made by an assistant who did not know the purpose of his measurements, and who was unfamiliar with the apparatus.

Test 1. Reading every 20 sec. for 10 min. Steady state.
Average reading, 999 mm. Highest, 1002 mm. Lowest, 995 mm.
Max. variation from mean, .4 of 1%. Ave. var. from mean, .14 of 1%

Test 2. Reading deflection for same density over 90 times, taking zero and resetting telescope between each reading, not moving plate.
Average reading, 1004.6 mm.
Highest reading, 1007.0 mm.
Lowest reading, 1001.0 mm.
Max. variation from mean, .36 of 1%.
Ave. variation from mean, .08 of 1%.

Test 3. Reading deflection for same density over 36 times, taking zero and resetting telescope, and removing and replacing plate between each reading.
Average reading, 1041.1 mm.
Highest reading, 1048.0 mm.
Lowest reading, 1031.0 mm.
Maximum variation from mean, 1%.
Average variation from mean, .45 of 1%.

These tests show that inaccurate settings of the plate produce errors seven times as great as those due to the densitometer itself. Such errors would of course be present in any type of physical photometer, and it is assumed that it is as easy to calibrate the deflections of the galvanometer in terms of light intensity on the thermocouple as it is to calibrate the wedge in the null method.

The curve in Fig. 3 was made with the running densitometer. The slight variation in some of the horizontal lines is not due to densitometer errors, but to specks and unevenness frequently present on spectrum plates.

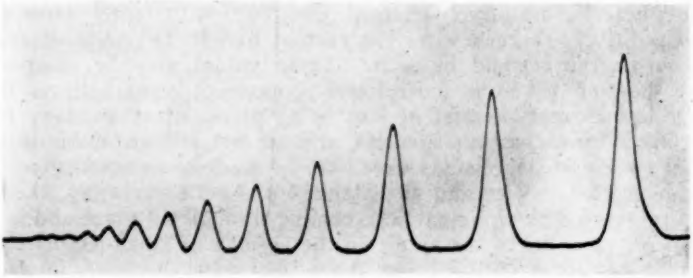

FIG. 3. *Densitometer tracing of a spectrum plate showing the potassium principal series in absorption, beginning with n=7, made by the improved direct-reading thermo-electric densitometer.*

While the form of instrument described is very convenient, the ultimate place for a densitometer would seem to be on a comparator for measuring wave-lengths. In this way the observer could measure the density of a line at the same time he measured its wave-length; he could also set in the exact middle, or on the center of gravity of a line much more accurately than with the eye, by watching galvanometer deflections as the slit crossed it. The thermocouple could be used in a holder no larger in diameter than a pencil, and an optical system could readily be devised to permit of light traversing the plate for its density measurement, and its viewing by the eye, at the same time. With one telescope to observe the plate, and another to read the galvanometer the combined comparator and densitometer would be an ideal instrument.

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NOVEMBER 7, 1924.

Discharges from pointed and curved Electrodes.—Experiments were performed in air at one atmosphere pressure (in some instances at lower pressures) one electrode being a wire with pointed or rounded end, the other another such wire or an extended plane. Attempts to follow the luminosity of the discharge with the eye as the current was decreased led to the conclusion that it gradually faded into invisibility without any sudden vanishing point or any abrupt correlated change in the current or voltage of the discharge; in other words the presumption is that the invisible discharges of exceedingly low current-strength do not differ in any qualitative way from the feebly luminous ones of somewhat greater currents, but only in that they are too faintly radiant for the eye to perceive. The least current at which the discharge was seen was $3 \cdot 10^{-9}$ amp., with a wire only 0.17 mm in diameter as negatively-charged electrode; with larger wires and also positively-charged wires the current had to be made stronger before anything could be seen. These values may be compared with those of Oelkers at much lower pressures. Zeleny believes that these low currents consist of ions being produced at a steady rate in the air by extraneous agencies, and are not self-sustaining in the usual sense. Measurements were likewise made upon the current between a pointed wire and an extended plane 1.5 cm away, the air being traversed by alpha-particles coming through the plane and moving nearly parallel to the wire. In the absence of alpha-particles the current was imperceptible below about 5000 volts, thereafter mounted with exceeding speed; when alpha-particles were admitted there was a perceptible current at the lowest voltages (presumably the ions produced by the rays) which remained constant up to 2000 volts or more and then began to increase very rapidly. Presumably this latter increase was a case of ionization by collision manifesting itself; but it depends on the sign of the P.D., setting in at a higher voltage and much more suddenly when the wire is negative than when it is positive. These deviations from the simple consequences of Townsend's theory may be due exclusively to the variation of field strength across the gap; an explanation on this basis is proposed. It is interesting that the currents due to alpha-ray ionization, below the voltage at which ionization by collision begins, are much higher than the currents in the luminous discharges just mentioned; yet visible light does not appear until they are augmented by collision-ionization. This is attributed to the high concentration of the ions at particular regions in the luminous discharges. Very distinct microphotographs of the luminous discharge from electrodes of various curvatures and each polarity are reproduced, and show the striking difference between the sheath-like glow on an anode and the fan-shaped brush diverging from a cathode. The Crookes dark space was discernible on the originals, and further information on the manner in which the phenomena change with pressure is promised —[J. Zeleny, Yale; Phys. Rev. *24*, pp. 255-271; 1924.]

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SPECTROPHOTOMETRY

REPORT OF O. S. A. PROGRESS COMMITTEE* FOR 1922-3

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* The Progress Committee on Spectrophotometry for 1922-3 consists of the following members: K. S. Gibson, Bureau of Standards, Chairman; H. P. Gage, Corning Glass Works; C. W. Keuffel, Keuffel and Esser Co.; A. H. Pfund, Johns Hopkins University; and A. G. Worthing, Nela Research Laboratory.

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I. INTRODUCTION

1. SCOPE OF THE REPORT

It has been suggested[1] that the reports of the various Progress Committees of the Optical Society of America should cover the following general lines of activity—(a) the preparation of yearly reports on progress in the particular field involved, (b) the preparation of reports dealing with the total status of the branch of optics concerned, (c) the compilation of constants and other valuable data needed by workers in the given field, (d) the tentative formulation of improved standards and definitions,—although the precise conception of the work of each committee has been left to the chairman of that committee.

In general, it is the purpose of this report to treat the subject of spectrophotometry under these headings. This being the first report, however, it necessarily must be different in nature from a mere progress report. It is hoped rather that it may serve as a basis for future progress reports. With this in view, the total status of the science has been briefly considered. Of necessity, this treatment has consisted largely of a study and exposition of methods and apparatus, rather than a compilation of constants or standards. A consistent nomenclature is highly desirable, and a section has been devoted to definitions of useful terms compiled largely from the closely related subjects of photometry

Note: The bold-face numbers within parentheses (followed occasionally by page references) refer to the Bibliography, Section VIII, at the end of the paper.

[1] Letter of Feb. 7, 1923, Pres. L. T. Troland to chairmen of Progress Committees.

and colorimetry; but the remainder of the report is devoted almost exclusively to a discussion of the underlying principles and methods of spectrophotometry, with the object of assisting those relatively unfamiliar with the subject to use the instruments and methods intelligently and correctly. The report is in no sense exhaustive. It is rather an attempt to set forth the least that should be known by those interested. Future reports, in addition to describing progress, may go more deeply into any part of the subject that may prove desirable.

Spectrophotometry may be defined as the visual measurement of relative radiant energy as a function of wave length or frequency. This energy may be that emitted by incandescent or other light sources, or it may be that transmitted, absorbed, or reflected by transparent or absorbing materials. Primarily, therefore, this report comprises a discussion of the methods of making such visual measurements. However, other methods than visual—for example, photographic, photoelectric, and radiometric—are often used in the visible region of the spectrum, especially for transmissive or reflective measurements, and of necessity in the ultra-violet and infra-red regions where the eye can no longer be used. Without intending to encroach on the subject of spectroradiometry, therefore, these auxiliary methods, as used to supplement and extend the visual methods in the spectral measurement of transmission or reflection, may properly be included in this report.

2. APPLICATIONS OF SPECTROPHOTOMETRY

The general purposes of spectrophotometry have been noted above; viz., the determination of spectral emissive, transmissive, and reflective characteristics. Such determinations, in the visible, furnish a basis of color specification which is unique and fundamental, in that the stimulus of the color may thus be completely specified. Such specification is independent of material color standards and of abnormalities of the observer's chroma vision—to one or both of which limitations all so-called colorimetric methods are in greater or less degree liable.[2]

As a means of study and analysis of the physical properties of materials or sources which determine their colors, spectrophotometric or spectroradiometric methods are absolutely necessary and colori-

[2] The relation between spectrophotometry and colorimetry has been treated in the Reports of the Colorimetry Committee (**1**;**4**). The fundamental nature of color specification based upon spectrophotometric data is readily granted by experts in color (**4**, p. 574; **119**, p. 700; **120**, pp. 73-75; **121**, p. 41; **123**, p. 42). The reasons that colorimeters and colorimetric methods have, nevertheless, been so extensively used is that they are often simpler and speedier of application and the results may be more readily interpreted as color (*Cf.* Sec. II-5 and 6, and Sec. VII-1).

metric methods totally inadequate. By extension into the ultra-violet and infra-red, as well as in the visible, such methods afford an invaluable means in the investigation of many problems of practical and theoretical interest—the analysis, structure, and purity of chemical compounds of wide variety, the suitability of so-called eye-protective glasses, the optical action of photographic, photometric, and other filters for isolating certain spectral regions, and so on.

The applicability of the various auxiliary methods for measurements in the visible spectrum is discussed in Section VI. It may be noted here that the extraordinary range of sensibility of the eye enables it to be used for measurement where these other methods would be inconvenient or impossible of application. A visual method is also logical as a means toward color specification, although handicapped in the blue end of the spectrum, which in spite of its low visibility has a marked influence on color.

Finally, spectrophotometric methods have direct application in the various investigations in psychophysical optics, such as the visibility of radiant energy, hue sensibility to wave length difference, etc., and are employed in the construction and use of colorimeters and other optical instruments.

These various applications, it is believed, furnish abundant justification for a report of this kind. If more were needed, it might be found in the fact that such a review of the subject has not, with possibly one or two exceptions (**89**; **90**), been recently attempted. It is hoped, therefore, that this outline—for it is little more than that—will bring the subject up to date and prove of assistance to the student or commercial worker who is beginning the study or use of spectrophotometric methods, perhaps also to some extent to the expert in this field of investigation.

II. NOMENCLATURE

It should be obvious that a clear, definite, and consistent nomenclature is not only an aid but a real necessity in the effective presentation of any subject. Because of the close relation of spectrophotometry to the sciences of colorimetry, photometry, radiometry, and spectrometry, most of the terms desirable for this report are found well defined in papers or reports on those subjects. The present section is, then, a compilation of terms already in use, selected with special reference to the needs of spectrophotometry. Naturally, a few differences of concept or definition are to be found among the various systems proposed

by different authors or committees. These will be noted and a tentative choice made for the purposes of this report.

The report of the O. S. A. Colorimetry Committee for 1919, I. G. Priest, Chairman (1), and a paper by Ives (5) have furnished most of the material for the nomenclature set forth herein. The terminology used is also largely in accord with that adopted by the Illuminating Engineering Society (6) so far as common ground is covered. Other references are given in the bibliography, (2; 3, 28).

1. RADIATION AND ILLUMINATION

In spite of the fact that illumination and its measurement, photometry, have been developed in much greater detail, so far as methods and terminology are concerned, than have radiation and radiometry, it is logical to consider the former as a special case of the latter, the eye being the particular kind of radiometer involved (a null instrument) and the visibility function expressing the relation between the various radiational and illuminational quantities. This is brought out in Table 1. The following definitions and remarks may be noted in connection with the table:

Radiation is the process by which energy is propagated through space, the possibility of propagation being unconditioned by the presence of matter (although the speed and direction of propagation, as well as the amount of energy transferred, may be thus affected). Strictly speaking, the term should not be used to express the "thing radiated," as is often done in expressions such as "radiations of a certain wave length" or "radiations transmitted or absorbed." For the science of radiation, the term *radiatics* has been suggested. *Radiant energy* is that which is transferred by radiation. Like any form of energy, it may be expressed in energy units, such as the erg or joule. *Radiant power* is the time rate of transfer of energy by radiation. Like any form of power, it may be expressed in power units such as the watt. This term has been internationally designated by the expression *radiant flux*.

If there be a source of radiant energy, the *radiant emissivity* is the radiant power per unit area of the surface. The *radiant intensity* in any direction from the source is the radiant power per unit solid angle in that direction.

If there be a surface emitting, transmitting, or reflecting radiant energy, the *radiance* of that surface in any direction may be defined either as: (a) The radiant intensity per unit of projected area in that

direction, or (b) if there be perfect diffusion, the radiant power from a unit area of the surface.

TABLE 1.
Radiation and Illumination

Radiation	Symbols and Defining Equations	Fundamental Units		(Lumination)*	Symbols and Defining Equations	Fundamental Units	Remarks
radiant energy	E	joule, erg		light (luminous energy)	$\int L\,dt$	lumen-hour	
radiant power radiant flux	$P=\frac{dE}{dt}$	watt		(light) (luminous power) luminous flux	L	lumen	4π lumens are emitted by a source of 1 candlepower
radiant emissivity	$\frac{dP}{da}$	watt per sq. cm.		luminous emissivity	$\frac{dL}{da}$	lumen per sq. cm.	
radiant intensity	$\frac{dP}{d\omega}$	watt per steradian		luminous intensity	$\frac{dL}{d\omega}$	candle =lumen per steradian	
radiance	$\frac{dP}{d\omega da\cos\theta}$	watt per ster. per sq. cm. projected area		brightness	$\frac{dL}{d\omega da\cos\theta}$	candle per sq. cm. projected area = lumen per ster. per sq. cm. projected area	1 lambert = 1000 millilamberts = $1/\pi$ candle per sq. cm.
irradiation	$\frac{dP}{da}$	watt per sq. cm. (incident)		illumination	$\frac{dL}{da}$	lumen per sq. cm. (incident)	1 lumen per sq. meter = 1 meter-candle = 1 lux = 0.0001 phot
radiometry				photometry			
spectroradiometry				spectrophotometry			

Visibility—spectral luminous efficiency—$V_\lambda = L_\lambda/P_\lambda$. The unit is the lumen per watt.

* Logically, this term should replace illumination as a name for the science.

If radiant energy be incident upon a surface, the *irradiation* of that surface is the radiant power per unit of intercepting area. (The term *specific irradiation* has also been suggested for this quantity, with irradiation to be defined as the total power incident upon that surface.)

Radiometry is the measurement of radiant energy or radiant power; *spectroradiometry*, this measurement as a function of wave length or frequency.

Light[3] is radiant energy multiplied by the visibility of the radiant energy. The time rate of transfer of light is internationally defined as *luminous flux*. Light, which is the stimulus, should not be used for color, which is the sensation. The expressions "ultra-violet light" and "infra-red light" are misnomers.

The above definition serves to define *visibility* as well as light. Visibility may be expressed absolutely in lumens per watt. It is a function of wave length or frequency and is often used relatively, the maximum being taken as unity. Standard values of relative visibility are given in Table 6. These are standard only under certain conditions. They are subject to considerable variations with changes in the size of photometric field, with changes in brightness, and with different individuals.

Relative light values are often called *relative luminosities*. In particular, the *luminosity curve* expresses the product of the values of spectral energy by visibility.

The terms *luminous emissivity*, *luminous intensity*, *brightness*, and *illumination* (or *specific illumination*) are to be defined strictly after the manner of the analogous terms on the left side of Table 1, replacing radiant power by luminous flux and the watt by the lumen. Because of the earlier and more common use of the photometric terms a more varied nomenclature has been developed so far as the units are concerned, as is noted in the table. For further details reference should be made to the reports on this subject issued by the I. E. S. (**6**) and the O. S. A. (**3**).

Photometry is the science and art of the measurement of light. *Spectrophotometry* is photometry as a function of wave length or frequency, and as already defined serves also in the spectral measurement of relative radiant energy.

2. SPECTRAL TERMS

The *spectrum* is an optical arrangement of radiant energy with respect to wave length or frequency. *Spectral distribution* of radiant

[3] The word light has been commonly used to designate the product of radiant power by visibility as well as radiant energy by visibility. Indeed, in this report, where light is considered as the adequate stimulus of color, the word is used in this sense. The unit employed in the designation of absolute visibility, the lumen per watt, is also in accord with this usage. Nevertheless, it seems best to define light primarily as above, considering it as the luminous entity which is emitted, absorbed, reflected, etc., analogous to radiant energy.

energy, light, etc., is a function expressing, analytically or graphically, the relation between the quantity in question and wave length or frequency.

There are several wave length units—the micron, μ, the millimicron, $m\mu$, and the Angstrom, A. (0.001 mm = 1 μ = 1000 $m\mu$ = 10,000 A.) All have had quite general use, the Angstrom being ordinarily used where there are four or more significant figures. The symbol, $\mu\mu$, sometimes called the micromillimeter, has been largely used for the millimicron, but this is inconsistent with the usage of μ to denote one millionth.

Frequencies are expressed in vibrations per second and in fresnels, f. ($1\,f = 10^{12}$ vib./sec.) The fresnel is ordinarily the more convenient. For example, the frequencies for 400, 600, and 1000 $m\mu$ are closely 750, 500, and 300 f, respectively. Another quantity much used in place of frequency is the "wave number." It is the number of wave lengths per centimeter of path in vacuo.

Radiant energy of a single wave length or frequency, actual or approximate, such as is emitted by sources of line spectra or transmitted by narrow spectrometer slits, is called *homogeneous*. Radiant energy that is not homogeneous is called *heterogeneous*. *Monochromatic* has been widely used in the sense of homogeneous as just defined; but the root, chroma (*Cf.* Sec. II-5), is commonly used in a different sense, as in dichromatic filters, trichromatic vision, heterochromatic photometry, etc.

3. TRANSMISSIVE TERMS

This report does not undertake the discussion of diffuse (or spread) transmission, which subject, along with diffuse reflection should properly be considered by the Reflectometry Committee. Terms relating to rectilinear transmission, however, of fundamental importance in spectrophotometry and colorimetry, are defined in this section, Tables 2 and 3. They are substantially the same as have been used in the colorimetry section of the Bureau of Standards for several years.

4. REFLECTIVE TERMS

As in the case of diffuse transmission, the present report, pending definite recommendations of the Reflectometry Committee, will not attempt a detailed discussion of reflective terms. It may be noted, however, that two types of reflection are of common occurrence, known as diffuse and specular, a combination of these two being often called spread reflection.

TABLE 2.

Terms Relating to the Rectilinear Transmission of Homogeneous Radiant Energy through a Homogeneous, Isotropic, Non-metallic Medium in the Form of a Plate with Plane, Polished, Parallel Surfaces Perpendicular to the Direction of Propagation.[a]

Let: b = distance between the bounding surfaces
E_1 = radiant energy incident on the first surface
E' = radiant energy reflected by the first surface
E_I = radiant energy transmitted by the first surface
E_2 = radiant energy incident on the second surface
E'' = radiant energy reflected by the second surface
E_{II} = radiant energy transmitted by the second surface

Then:

$\rho = E'/E_1 = E''/E_2$	= *reflectance*
$\tau = E_I/E_1 = E_{II}/E_2$	= *admittance*
$T = E_{II}/E_1$	= *transmission*[b]
$\mathsf{T} = E_I/E_1$	= *transmittance*
$t = \sqrt[b]{\mathsf{T}}$	= *transmissivity*[c]
$O = 1 - T$	= *obstruction*
$A = 1 - \mathsf{T}$	= *absorptance*
$D = -\log_{10} T$	= *density*
$i = -\log_e t$	= *transmissive exponent*
$k = -\log_{10} t$	= *transmissive index*

[a] In deriving these relations, multiple reflections between the bounding surfaces have been neglected. This is permissible for a single plate of the ordinary refractive index for non-metallic substances. It is not permissible in case ρ has a high value.

[b] In addition to this restricted meaning of transmission, the term is also used, as is absorption and reflection, to denote a general subject or phenomenon.

[c] This relation is known as Lambert's law.

TABLE 3.

Terms Relating to a Substance in Homogeneous Solution in a Solvent Contained in a Cell with Plane, Parallel Sides Perpendicular to the Direction of Propagation, the Propagation through the Cell and Solution Being Rectilinear.

Let: T_{sol} = transmission of a given cell containing the solution
T_{sov} = transmission of the same (or a duplicate) cell containing pure solvent

Then:[a]

$$\mathbf{T} = \frac{T_{sol}}{T_{sov}} = \frac{\mathsf{T}_{sol}}{\mathsf{T}_{sov}} = \textit{transmittancy}$$

$\mathbf{t} = \sqrt[bc]{\mathsf{T}}$ = *specific transmissivity*[b]
where c = concentration of the solution
and b = thickness of the solution

$\mathbf{i} = -\log_e \mathbf{t}$ = *specific transmissive exponent*
$\mathbf{k} = -\log_{10} \mathbf{t}$ = *specific transmissive index*[c]

[a] The symbols $\mathbf{T}$, $\mathbf{t}$, $\mathbf{i}$, and $\mathbf{k}$ are distinguished from the terms T, t, i, and k, of Table 2, in handwriting and typewriting by using the underscore, and **in printing by the use of bold face type.**

[b] This relation is known as Beer's law. In many cases it is only approximate.

[c] This term has been commonly designated as *extinction coefficient.*

Spread reflection is that in which the reflected radiant energy is nonuniformly distributed with respect to the normal to the reflecting surface. This is the usual case of reflection, and falls between *perfect diffusion*, in which the intensity of the reflected energy in any direction varies as the cosine of the angle between that direction and the normal to the surface, and *specular* reflection, in which the angle of reflection is equal to the angle of incidence and there is no diffusion.

Reflectance (as noted incidentally in the definitions of transmissive terms) is the ratio of reflected to incident radiant energy. The term *reflectivity* is probably also desirable, meaning the reflectance for infinite thickness of the reflecting substance. The reflectance of thin metallic films and diffusing media varies appreciably with thickness.

5. COLOR AND LIGHT

Color is the sensation due to stimulation of the optic nerve. While this stimulus may be of various kinds—electrical, mechanical, etc.—the ordinary stimulus is light. Color is thus subjective, light objective. *Colorimetry* is the science and practice of determining and specifying colors by reference to the stimuli and conditions which evoke them.

Color has three attributes—brilliance, hue, and saturation—which may be correlated with measureable light quantities as in Table 4. Definitions of the various terms follow:

TABLE 4.
Color and Light

Color (subjective)	evoked by	Light (objective)
Brilliance		light or brightness
hue*		dominant wave length
saturation*		purity

*The quality of a color resulting from its hue and saturation is called its chroma.

Brilliance is that attribute of color without which color cannot exist, the attribute in respect of which all colors may be classified as equivalent to one or another of a series of grays of which black and white are the terminal members.

Hue is that attribute of color in respect of which it differs from gray, the attribute in respect of which colors may be classified as reddish, yellowish, greenish, or bluish.

Saturation is the distinctness or vividness of hue.

The property of color due to its hue and saturation is called the *quality* of the color, or its *chroma*.

No hue can be experienced without brilliance, but brilliance may be experienced without hue.

Light and brightness have already been defined. The measureable term often used in this connection is the *relative brightness*, as given by the integral light transmission or the integral light reflectance of materials, which are ratios largely independent of the absolute brightness as determined by the intensity of the incident light (although they will vary with the spectral distribution of the light).

Dominant wave length is the wave length of the homogeneous light which must be mixed with white light to match the color to be specified.

Purity is defined as the ratio of homogeneous light to homogeneous light plus white light in the mixture just referred to. *Impurity* is equal to unity minus the purity.

White, or *gray*, may be defined as a color without hue. For the measurement of purity after the above definition a standard spectral distribution of radiant energy evoking this hueless color is highly desirable. Pending definite standardization, average noon sunlight and the Planckian distribution at 5000° K are being used (Table 7), or, for experimental purposes, the light from incandescent sources through "daylight" filters at a color temperature (for the combination) of approximately 5000° K.

6. SPECIFICATION OF COLOR

A color may be specified by reference to stimuli in the following ways:

(1) By specification of a stimulus empirically found to evoke the same color.

(2) By specification of the identical radiant energy actually evoking the color.

Instruments for the specification of color empirically, (1), are usually called *colorimeters*; those which measure the spectral distribution of radiant energy, (2), are called *spectrophotometers* or *spectroradiometers*.

It is, of course, not the function of this report to discuss colorimeters. It may, however, be noted that the specification of color by determining the dominant wave length, purity, and brightness—called monochromatic or homo-hetero analysis—seems the most logical and most readily interpreted of any of the colorimetric methods. These three physical quantities may be measured directly or they may be computed by methods outlined by the Colorimetry Committee and by Ives (*Cf.* Sec.

VII-1 and 2). When measured directly, they may be subject to uncertainties arising from abnormalities of the observer's chroma vision. Since spectrophotometric or spectroradiometric measurements are unaffected by such abnormalities, the transformation of such data into the monochromatic system will give such specification in standard form independent of these abnormalities. This ideal result can be reached, however, only approximately, pending further statistical determination of the "three excitations" entering into the transformation.

It may again be emphasized that any colorimetric method is of value only as a specification of the color; it is of little or no value as a means of analysis of the light or radiant energy evoking the color. It may be further noted that: (a) the fundamental reference standards of colorimetry are light sources of specified spectral distribution of radiant energy, (b) the most fundamental specification of the color of a transparent plate is its spectral transmission, (c) the most fundamental specification of the color of an opaque object is its spectral reflectance.

III. Spectrometry

Every spectrophotometric apparatus consists essentially of two parts: (a) the spectral dispersing system, and (b) the photometric system. Spectral dispersion is usually effected by a prism system, although grating systems have been used. The photometric system consists ordinarily of a uniformly illuminated two-part photometric field with means available for varying the brightness of one or both parts in a continuous and known manner. It is obvious that any intelligent understanding of spectrophotometric apparatus and methods is dependent upon a knowledge of the theory and use of the spectrometer and the photometer as separate instruments.

It is impossible, however, in a report of this kind to discuss adequately either of these subjects. The attempt has been made, therefore, in Sections III and IV to touch only upon the various aspects of each science which have direct application to spectrophotometry. The various references will be sufficient to lead one into a thorough study of the subjects.

1. ESSENTIAL PARTS OF A SPECTROMETER

The essential parts of a spectrometer are illustrated in Fig. 1,* wherein are outlined three kinds of spectrometer which have formed the bases of various spectrophotometers. Each instrument consists

* The Committee is indebted to Mr. C. L. Snow of the Bureau of Standards for the excellent appearance of the illustrations given in this report.

of a collimating telescope or collimator C, a spectral dispersing prism or grating P, and an observing telescope T. In addition to a lens, as shown, the collimator and telescope each carry a slit, S_c and S_t,[4] respectively. The refracting edge r of the triangular prism, or its equivalent in the other types, must be perpendicular to the plane containing the axes of the telescope and collimator. The slits must also be vertical to this plane and must be at the focal distances of the lenses.

Types A and B are two common forms of prism spectrometer. In type A, a 60° prism of flint glass is ordinarily used. The collimator and prism are fixed and the telescope is rotated about the axis of the prism. This type of spectrometer may be so designed, however, that the tele-

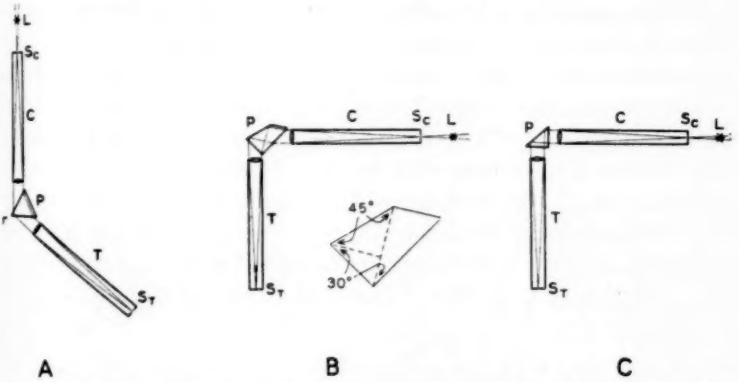

FIG. 1.—*Three types of spectrometer that have formed the bases of various spectrophotometers. Types A and B are prism instruments, type C a grating instrument.*

scope and prism are both movable, the prism being kept automatically at minimum deviation as the telescope is rotated. Type B is known as the constant deviation spectrometer. The collimator and telescope are permanently fixed at right angles to each other, and the prism is rotated. As may be noted from the insert, this quadrangular prism is equivalent to two 30° prisms and a totally reflecting prism. The grating spectrometer, type C, is also a constant-deviation instrument, the collimator and telescope being fixed at right angles and the prism rotated. The grating is a replica placed upon one of the faces of the totally reflecting prism.

[4] Instruments not designed primarily for spectrophotometry often have the ocular slit S_t omitted. In such cases the eye piece usually carries an adjustable diaphragm which may be made to serve as a slit, or may carry cross hairs by which the location in the spectrum is determined.

2. SIMPLE THEORY

If a source of light is placed at L before S_e and the instrument is in proper adjustment, a spectral image of S_e is formed in the plane of S_t at right angles to the axis of the telescope. The light from L entering S_e has been rendered parallel by the collimator lens; this parallel beam by its passage through the prism has been deviated, the angle of deviation varying with the wave length or frequency of the components of the light; the resulting dispersed beam is brought to a focus by the telescope lens and forms a spectrum at the slit S_t. The wave length or frequency of the light transmitted by S_t depends upon its position in the spectrum.

This spectrum may be examined with a magnifying lens or system of lenses known as the eyepiece. This is focused upon S_t, and if the adjustments are correct the spectrum will also be in focus. If a source of homogeneous light such as the mercury arc or sodium flame is placed at L, "lines" will be seen at certain places in the spectrum. These lines are the spectral images of slit S_e and their dimensions will vary with those of S_e. The spectral lines, characteristic of any given source, will be separated by dark intervals (*Cf.* Fig. 2). If L is a source of heterogeneous light such as an incandescent electric lamp or acetylene flame no spectral lines will be visible, but the overlapping images of S_e will result in what is known as a continuous spectrum, all the various hues from red to violet (excepting the purples) being present in gradual transition from one to the other.

If the eyepiece is removed and the eye looks directly into the slit, the prism or lenses may be seen. If L is not too near S_e, a more or less poorly defined image of it may also be visible. In any case the brightness will vary with the width of either S_e or S_t (provided the latter is smaller than the pupil of the eye), but the appearance will otherwise be largely independent of such variations. If L is a source of uniform brightness of size sufficient to fill the solid angle subtended by the collimator lens and S_e, its image will give a uniform field filling the telescope lens, unless its dimensions have been reduced by some other obstruction. Any marks, dust, or other irregularities on or within the lenses or prism, will be visible.

Either this uniformly illuminated field viewed by the eye directly through S_t or the portion of the spectrum viewed with the eyepiece may be made the basis of the photometric field, as explained later.

3. ADJUSTMENTS

Certain conditions to be fulfilled, if the instrument is to be in proper working condition, have already been mentioned. The following details, explanatory or additional, may be noted.

In some spectrophotometers no prism adjustment is possible, the makers building the prism permanently into its proper position. In others the prism must be adjusted as on the simple spectrometer. This includes proper location and proper leveling. The triangular prism, type *A*, should be adjusted for minimum deviation of the yellow Hg, He, or Na lines. The constant-deviation prism, type *B*, must be located properly on the axis of rotation to insure that all rays are at minimum deviation (**10**).

Most spectrophotometers have the slit heads adjustable along and around the axis of the collimator or telescope. The following simple procedure for focusing and alignment of slits will usually suffice:

(1) The telescope should be sighted upon some distant object (far enough away to insure sensibly parallel rays). The image of this object will be formed at the focus of the telescope lens and may be viewed with the eyepiece. The ocular slit should then be moved along the axis of the telescope until a position is found where both the image and the edges of the slit are in focus and there is no relative motion, or parallax, between them as the eye is moved from one side to the other. The slit is now in the focal plane of the telescope lens, and the distance from lens to slit should not thereafter be changed.

(2) The telescope is reinserted in the instrument (if removed) and the slit adjusted around the axis of the telescope until it is perpendicular to the plane of the telescope and collimator, care being taken not to change its distance from the lens. Inasmuch as this plane is usually horizontal or vertical, this adjustment is not difficult.

(3) With the telescope, prism, and collimator in position and a source of homogeneous light before S_c, the position of S_c should be adjusted until its image, as given by some spectral line and viewed with the eyepiece, is brought into exact focus with S_t (no parallax) and is parallel to it.[5]

[5] In prism instruments a curvature of the spectral line may be noted, especially if S_c is viewed at full length. Only the light from the center of S_c undergoes true minimum deviation. The central part of the line should, of course, be made parallel to S_t. It will also be found that the complete spectrum cannot be brought into exact focus by any single adjustment. The lenses for the usual visual instrument are achromatised for the range 486-656 mμ (C to F). If the instrument is focussed upon some line in this range, preferably in the yellow, it will probably be in focus at all wave lengths not only in this range but also throughout the red, but towards the shorter wave lengths the parallax between S_t and the spectral line will become increasingly noticeable.

(4) If the spectrophotometer has a second collimator, a similar adjustment must be made. This second collimator must also be adjusted so that the images of the two collimator slits for a given spectral line will have identical positions.

(5) All these adjustments should finally be made secure so that there will be no possibility of their changing.

While the slit width method of varying brightness is not to be recommended (*Cf.* Sec. IV-2-*A*), it is desirable that all the slits, on telescope as well as collimator, should be of the bilateral type—that is, opening symmetrically in both directions from the zero position—with a micrometer scale by which the slit width may be noted. The usefulness of spectrophotometers for many purposes is limited if such slits are not provided.

In addition to the above general adjustments, most instruments have further particular adjustments peculiar to the given type. These are noted to some extent in Section V.

4. SPECTRAL CALIBRATION

All spectrophotometers have a scale by which the position of slit S_1 in the spectrum may be noted. In some instruments this scale reads directly in wave length or frequency. In this case the calibration should always be very carefully checked over the range to be used. In other cases the scale is an arbitrary one and must be calibrated in terms of wave length or frequency.

In either case, suitable sources of homogeneous light should be available. The best sources are those having a few easily recognizable lines well distributed over the spectrum. Sources with a large number of lines, such as the iron arc, are practically useless and should be avoided —except in the case of the Fraunhofer lines of the sun's spectrum, which, in spite of the great number, include several intense and well distributed lines that are easily identified.

In Fig. 2 are given schematically the spectra of some of the most suitable sources, after the usual prismatic dispersion. In some cases where faint lines are easily identified, they have been included (as may be noted) along with the more prominent lines. The vacuum tubes and mercury arc are perhaps the most convenient to work with. It requires somewhat more care and technique to get good working spectra from the flame and bare arcs, but they may often be the only ones available. In some cases, where desirable, considerable increase

[1] Wave lengths are based on the International scale. Values based on Rowland's scale in some cases differ by 0.1 from the values given above.

[2] There are a great number of other fainter lines.

[3] Quartz or glass. With the former, other faint lines are practicable for use.

[4] These lines also appear in the arc spectra of the respective elements. The Na lines appear in all the flame or bare arc spectra. Cs has several faint lines in the orange and red.

[5] Many fainter lines in the blue not shown.

[6] Bare metallic arcs or carbons filled with salts of the metal.

[7] Cr has two pairs of easily identified triplets in the red but the spectrum is very complex in the blue.

FIG. 2.—*Schematic illustration of the spectral lines of some of the more suitable sources for spectrophotometric calibration. The relative positions are approximately those for a prism instrument. Faint lines are not shown except where easily identified.*

in brightness is possible by focusing the source upon the collimator slit. The ultraviolet radiant energy from the quartz-mercury arc and certain of the bare metallic arcs is very dangerous to the eyes. Prolonged exposure of the skin will also cause severe burn. Most glass of 2-mm thickness or more is an effectual protection against such arcs.

In case the lines of Fig. 2 prove inadequate for any reason, recourse may be had to any of the extensive atlases of standard wave lengths (**13**; **14**; **15**; **16**; **17**). In some of these will be found details of technique for producing the various spectra. It may be further noted here that the many lines of the neon vacuum tube are excellent for calibration in the orange and red regions with a grating spectrometer where the dispersion is much greater than in the prism instruments, and that the barium and calcium arcs are also good for general calibration although having more lines than could well be shown in the figure.

The values of Fig. 2 are given only to tenths of a millimicron; and, in general, it is entirely impracticable to attempt to calibrate a spectrophotometer more exactly than this. The problems and applications are much different from those in spectroscopy, where small fractions of an Angstrom unit may be significant. The slit widths ordinarily used in spectrophotometry include from 1 to 10 mμ. Moreover, it is impossible to keep the usual instrument in adjustment to a degree that would warrant a calibration finer than to tenths of a millimicron.

In general, this calibration should be made with the slit-widths not greatly different from those to be used in practice; and if any slit happens to be unilateral, care should be taken to secure the correct effective wave length when a source of heterogeneous light is used. It is also advisable to calibrate with the same lengths of slits as will be used, and take into account the effect of any curvature of the line upon the mean wave lengths transmitted by the telescope slit for a continuous spectrum.

Most experienced observers probably have their own technique of calibration which they prefer to any other. An excellent way, where bilateral slits are used, is to make the telescope slit slightly larger than the collimator slit and center the spectral line within the former. An aid to this is a luminous background upon which the edges of the line and the slit are clearly visible. The sun, a carbon arc, and to a less extent a metallic arc or the Hg arc, will furnish its own background, a continuous spectrum, upon which the lines will be visible. If the spectrophotometer has a second collimator, the continuous spectrum may be formed from an incandescent light placed in front of its slit.

If no background is available the jaws of the telescope slit may be illuminated externally. Other schemes will suggest themselves to the investigator.

If the instrument is one already reading directly in wave lengths or frequencies, a correction curve should be plotted—differences between observed and true values against true values. From this curve the instrument setting for any correct wave length or frequency may be obtained. (If the instrument were to be used as a spectrometer to locate spectral lines, the differences should be plotted against observed values.)

If the instrument has an arbitrary scale, wave length or frequency should be plotted as a function of the observed scale reading. The frequency curve has less curvature than the wave length one, and it is sometimes desirable to use it for this reason. It is often more useful, however, to plot a wave length calibration curve. If the wave lengths chosen are sufficiently numerous and well distributed it is an easy matter to draw a smooth accurate curve through the observed points, from which the scale reading for any desired wave length may be readily obtained.

It is sometimes desirable to have the equation of this curve, wave length λ against scale reading s, either for purposes of calibration or to form the derivative function $ds/d\lambda$, which is proportional to $d\theta/d\lambda$, called the dispersion, θ being the angle of deviation. Various formulas have been proposed to represent this curve for glass, but the only ones found suitable (11) are the empiric formulas,

(1) $$\frac{1}{s-s_0} = A + B\lambda \quad \text{(Hartmann Formula)}$$

(2) $$\frac{1}{s-1} = A + B\lambda^2$$

wherein A, B, and s_0 are constants to be determined. Three spectral lines in the case of (1) and two in the case of (2) are, of course, necessary and sufficient for the determination of these constants. They should be so chosen as to include the regions for which the equation is to be used, and in the case of formula (1) the three wave lengths should be fairly equally distributed. It is unsafe to use the formulas for much extrapolation.

The derivative function $ds/d\lambda$ may, of course, be obtained graphically without recourse to the equation, although it is difficult to get precise values by this method. Approximate values may also be

obtained experimentally by noting the difference in scale reading for two spectral lines close together.

In Fig. 3 are given typical curves for a glass-prism instrument. These include the wave length calibration curve, the dispersion curve, and the frequency calibration curve. Along the abscissas are also indicated the amounts of spectrum transmitted by a 0.20-mm slit. A knowledge of these effective slit widths is important in deciding upon the proper mechanical widths to use. The values are about the same for most spectrophotometers. They may be obtained by noting, for example, the number of scale divisions equivalent to the passage of one edge of a spectral line from one edge to the other of the ocular slit, the equivalent wave length or frequency interval being derived from the respective calibration curves.

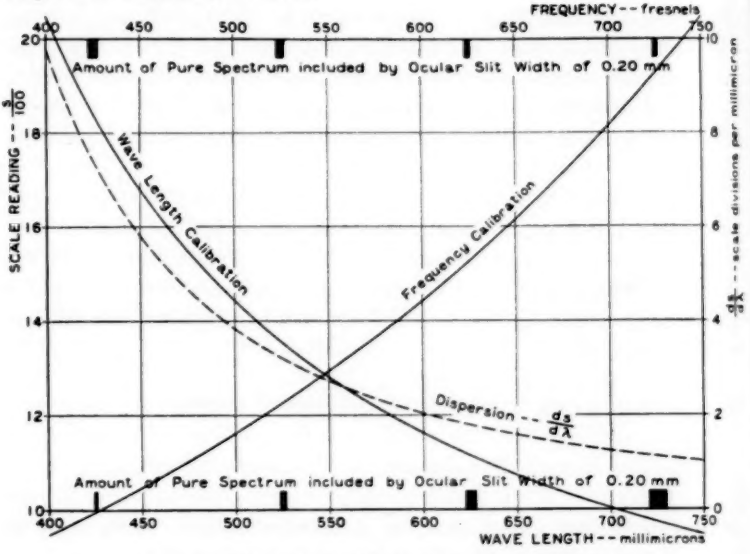

FIG. 3.—*Typical characteristics of prism spectrophotometers.*

5. INSTRUMENT-TRANSMISSION

It is of general interest, and occasionally is necessary, to know the spectral transmission, relative or absolute, of a spectrophotometric system. Some representative transmission curves are given in Fig. 4. The transmission of the instrument as a whole may be measured with another instrument (*Cf.* references, Fig. 4), or the transmission of the separate parts measured or computed.

In the case of a prism, the loss both by reflection and absorption may be considerable. That lost by reflection may be computed from Fresnel's law. If i and r are the angles of incidence and refraction, respectively, at any surface, then for light polarized at right angles to the plane of incidence the fraction of incident light reflected is $\frac{\sin^2(i-r)}{\sin^2(i+r)} = X$. For light polarized in the plane of incidence, the fraction reflected is $\frac{\tan^2(i-r)}{\tan^2(i+r)} = Y$. For ordinary unpolarized light the fraction transmitted will equal $\frac{1}{2}[(1-X)+(1-Y)]$. For two surfaces the transmission will equal $\frac{1}{2}[(1-X)^2+(1-Y)^2]$, and so on. This, of

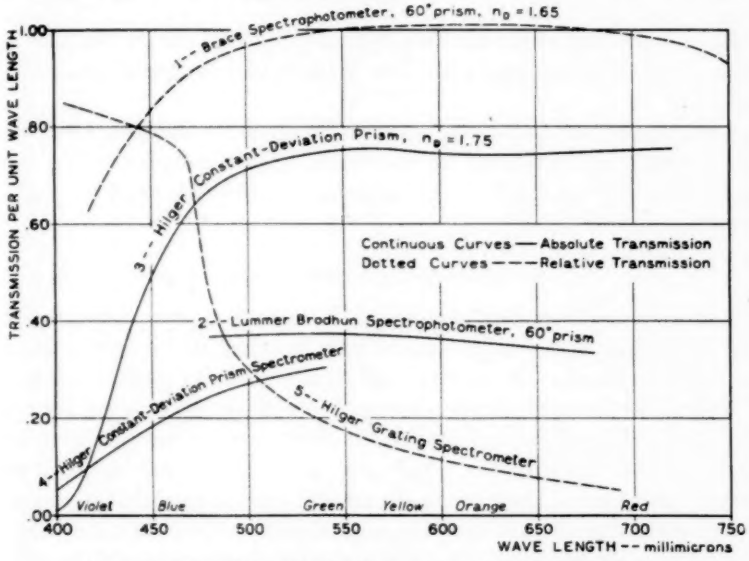

FIG. 4.—*Transmission of various instruments used in spectrophotometry.*

References: Curve 1—Reference 35, p. 139; Curve 2—Reference 34, p. 72; Curve 3—Bur. Stand. Test No. 33845; Curve 4—Reference 32, p. 89; Curve 5—Bur. Stand. Test, IV-3.

course, assumes constant values of i and r for the successive surfaces, which is true for a prism at minimum deviation or for a plate with parallel faces. For normal incidence at any surface the fraction of incident light reflected is $\left(\frac{n-1}{n+1}\right)^2$, where n is the index of refraction between the two media bounding the surface. This is a special case of either of the two formulas above. It may be used to compute the

approximate transmission of lenses and other glass surfaces of known index which do not absorb appreciably.

The transmittance of a prism (triangular at minimum deviation) is given by the equation (7)

$$\top = 0.4343 \frac{t^b - 1}{\log_{10} t^b},$$

where b is the length of the base of the prism and t is the transmissivity of the glass. In the case of the constant deviation prism, the expression becomes

$$\top = 0.4343 \frac{t^{2b} - 1}{\log_{10} t^{2b}} (t^{a+c-b}),$$

where b now represents the base of the smaller 30° prism, c the base of the larger 30° prism, and a the side of the totally reflecting prism (*Cf.* Fig. 1).

As actually used in the instrument, all of the prism is seldom used, but only that part subtended by the lenses. This complicates the expressions (12), but the error in neglecting this factor is small if the absorption is not large.

6. EXCLUSION OF STRAY LIGHT

All spectrophotometers have a certain amount of stray light present at any region of the spectrum, as may be noted if the light passing through the ocular slit is examined with a small hand spectroscope. Throughout the brighter part, however—viz, from about 510 to 660 mμ for a prism instrument and the usual incandescent sources—the relative value of this stray light is usually too small to introduce appreciable error. But beyond these limits the amount present increases more and more rapidly and becomes 100 per cent when the ultra-violet and infrared regions are reached. Its actual magnitude will depend on the type of light source being used, and will vary somewhat with the observer's visibility.

This stray light is a result of reflections from the sides of the collimator or telescope, if the diaphragm system is not perfect, and of scattering from the lens and prism surfaces due to dust or scratches upon them. "Ghosts" or minute spectra may also be visible if one looks directly into the slit. The obvious remedy for these troubles is to remove the causes, so far as possible, by the use of proper diaphragms and clean surfaces. That remaining may be measured and corrections applied, if necessary; or preferably, when possible, it should be elim-

inated by the use of proper ray filters over the ocular slit. The proper filter is one having high transmission at the wave length at which measurements are being made and high absorption of all the brighter parts of the spectrum. Illustrative stray light curves are given in Fig. 5, along with the transmission curves of the most suitable types of filter for its elimination. In addition to the references there given, a paper by Ives (**74**) on the subject will be found very helpful.

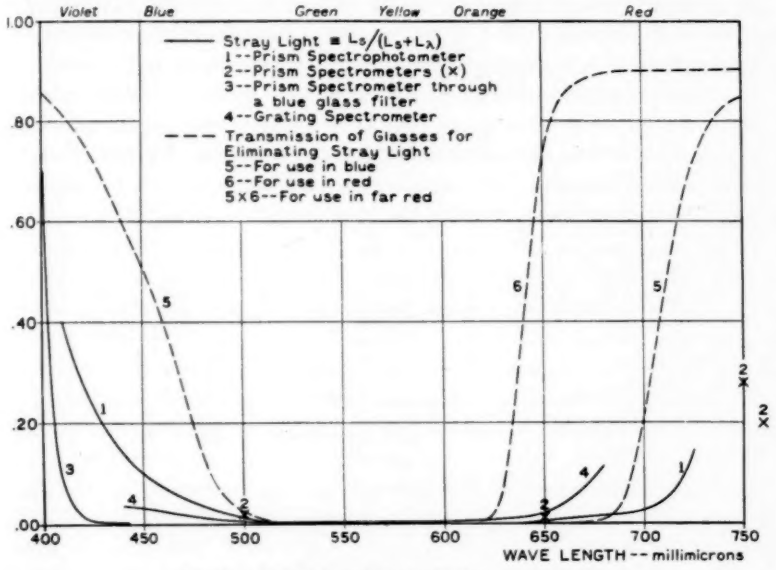

FIG. 5.—*Stray light and its elimination—typical data.*

References: Curve 1—Reference 35, p. 144; Points 2—Reference 34, p. 72; 33, p. 219; 31, p. 289; Curve 3—Reference 32, p. 88; Curve 4—Reference 124, p. 197; Curves 5 and 6—Reference 35, p. 144. Curves 5 and 6 are for Jena glasses—Curve 5 for Jena 3654, Curve 6 for Jena 4512. Similar glasses are made by the Corning Glass Works—Corning G585 is practically equivalent to Jena 3654, Corning G24 to Jena 4512.

IV. PHOTOMETRY

1. THE PHOTOMETRIC FIELD

The second of the two essential parts of any spectrophotometric apparatus is the photometric system. This, as noted at the beginning of Section III, consists of a uniformly illuminated two-part photometric field with means available for varying the brightness of one or both parts in a continuous and known manner. These conditions are

necessary because of the fact that the eye is essentially a null instrument, unable to estimate, except crudely, absolute or even relative brightnesses, but able to judge accurately as to the equality of two brightnesses when properly juxtaposed.

Five more or less common photometric fields used in spectrophotometry are shown in Fig. 6, the two parts of the field being labeled 1 and 2, respectively. The optical means of obtaining such fields are discussed in Section V in connection with the actual instruments. It may be noted here, however, that type I is that ordinarily obtained when an eyepiece is used, parts 1 and 2 representing portions of the juxtaposed spectra that are transmitted by the ocular slit or by the diaphragm in the eyepiece. The other fields, type II, are those commonly found with instruments where one looks directly into the ocular slit, the circumference being formed by the telescope lens, a diaphragm, or other means. Type II-*d* is commonly used in the contrast form.

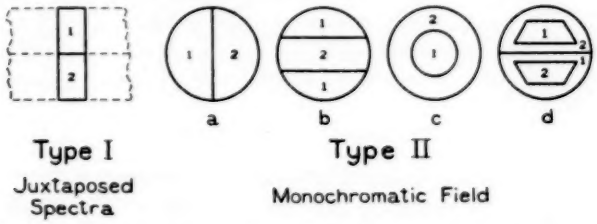

FIG. 6.—*Common types of photometric field used in spectrophotometry.*

2. METHODS OF VARYING THE BRIGHTNESS

The continuous and known variation of brightness essential to precise photometric work may be accomplished by a variation of the slit area itself, by polarization methods (within or without the instrument), or by variable distance or variable sector methods which vary the amount of light entering the collimator slit. Certain details connected with these methods are noted below. Other methods of limited value are also mentioned.

A. Variable Slit Width.—The amount of light entering the collimator may be controlled by varying the aperture comprised by the collimator slit. As a rule the length of the slit is fixed or only crudely adjustable, but the width is controlled by a fine micrometer screw. The brightness has usually been taken as proportional to the slit width as read on the micrometer drum. This method although often used in the past can seldom be considered other than an approximate one.

Its advantages consisting of ease of adjustment, the elimination of auxiliary apparatus, and the conservation of light, are offset by the following defects:

(1) The effective wave length with heterogeneous light varies with the width of a unilateral slit, and in only one place in the spectrum—the region of maximum luminosity—is the brightness even approximately proportional to the width.

(2) The bilateral slit is much superior to the unilateral—the effective wave length remaining practically constant as the width is changed—but in only two places in the spectrum is the brightness theoretically proportional to the slit width. These are at the points of inflection of the luminosity curve.

(3) The widely different slit widths necessary if the method is to have a suitable range introduces further uncertainties: (a) Diffraction at the edges of the slit (**76,** pp. 500-503; **78,** p. 245) makes the true zero scale reading difficult to determine, with the possibility of large percentage errors at small slit widths; (b) in certain parts of the spectrum the hue will change appreciably with a large change in width, even with the bilateral slits.

(4) Errors resulting from the impurity of the spectrum, present with all slits of finite width where a heterogeneous source is used (*Cf.* Sec. IV-4-*D*), increase rapidly with the slit width, and the correction is complicated where the width is being changed.

(5) The slit-width method can not be used with homogeneous light in spectrophotometers with eye piece and field of type I, Fig. 6, thus eliminating a valuable check upon measurements with the heterogeneous source.

Errors in the method may be reduced by the use of rotating sectors of fixed apertures or by other methods which reduce the range of slit widths necessary. They may still further be reduced by calibrating the slit-widths by these auxiliary methods, as has often been done (e.g., **64**;**80**). The calibration has to be made, however, at several wave lengths well distributed over the range of spectrum to be used. The troubles enumerated above have long been well known and early led to the development and use of the other methods described below. Except in very special cases the variable slit-width method is now seldom used.

B. Polarization Methods.—The various prisms made from calcite—the nicol, wollaston, and others—and transmitting beams of plane polarized light have been widely used in spectrophotometers. The

prisms are usually a part of the instrument and give all the ease and convenience of adjustment that the variable slit method does, but with none of its disadvantages. Polarization methods are wasteful of the light—the transmittance of a single nicol cannot be greater than 0.5—but the efficient artificial sources of light at present available make this objection of less weight than formerly.

Various combinations have been used. With two nicols in series, one being rotated, the brightness is proportional to the $\sin^2$ of the angle of rotation measured from the position of extinction; with three in series, the middle one being rotated, it is proportional to the $\sin^4$ of the angle, likewise measured. With the rochon or wollaston prism and analysing nicol, the $\tan^2$ relation forms the basis of the computation. The correctness of these relations should be verified in any particular case, as the polarizing action of nicol prisms is occasionally imperfect. These combinations will be further described in Section V-3, in connection with some of the actual instruments.

In some of the earlier instruments the polarization at the surfaces of the dispersing prism was disregarded with consequent serious error. With the proper construction, however, this error may be eliminated, except possibly where the light is polarized before reaching the instrument. In that case, as may happen for example in the spectrophotometry of light sources or in transmissive measurements on crystals, due precaution must be observed in the interpretation of results. This is true for practically all spectrophotometers, whether nominally polarization instruments or not.

Special tables and slide-rules are available which greatly simplify the otherwise laborious computations resulting from the use of polarization methods.

C. Variable Distance.—The inverse-square law is one of the fundamental relations of photometry. Given a point source, the amount of light intercepted by a given area must be inversely proportional to the square of its distance from the source. Since all sources depart appreciably from this hypothetical point-source condition, a certain amount of approximation would seem inevitable, but if the distances used are suitably large relative to the dimensions of the source, the errors involved will be less than the photometric precision. A minimum distance of 30 times the diameter of the source will introduce an error not greater than about 0.1 per cent. For shorter distances, if the highest accuracy is desired, the brightness should be taken as inversely proportional to the square of the distance as ordinarily measured plus the square of

the radius of the source. Formulas for the illumination from a radiating disk have been derived (**19**; **23**).

D. Variable Sectored Disks.—Talbot's law (**18**) of the rotating sector states that when a beam of light is periodically interrupted as by a rotating sectored disk of aperture $\alpha°$ at a frequency great enough to eliminate flicker, the eye integrates the resulting transmitted light in such a way that its apparent intensity is equal to $\alpha/360$ of the original intensity.

Rotating sectors of fixed angular aperture have long been in use as an aid to other methods of varying the brightness. To be the sole means of such variation, however, the aperture must be accurately adjustable while the sector is rapidly rotating. Various types have been devised. The Brodhun sector (**20**) consists of a pair of rotating rhombs which carry the beam of light across a sector whose angular aperture may be varied. This sector is convenient to use but is the most wasteful of light, as it transmits only about 0.4 of the incident light at the maximum opening (sector 0.5, rhombs 0.8). It is also slightly selective in its transmission, but this is no objection for many kinds of work. The sector designed by Hyde (**78**) is unique in having the angular aperture variable from zero near the center to about 0.9 near the circumference. Variation in brightness is secured by moving the sector bodily at right angles past the collimator slit. This sector is the least wasteful of light of any devised, but must be calibrated in position. It can be used only before a narrow aperture such as a collimator slit. Like the other sectors noted below, it is non-selective in its transmission; but unlike any other, this one has the advantage that the percentage change in transmission of the sector, corresponding to a given displacement on the reading scale, is practically constant for all transmissions.

Other types of variable sector have been devised by Pfund (**26**), Keuffel and Esser (**92**), Ives (**29**), and others, all of which consist of two sectors in series, rotating at the same rate, whose relative position may be altered while in motion by various mechanical arrangements. The K. and E. sector is briefly described in Section V-4-(b).

E. Other Methods.—Although the four methods above noted have been the most widely used, several other methods of continuously varying the brightness are available. In some the law of variation is known exactly, in some only approximately, while others are entirely dependent upon an empiric calibration. The following may be noted:

(1) Lambert's law of the variation of transmittance with thickness, $T = t^b$, makes possible a method of measuring the transmissive con-

stants of a liquid. Variation of brightness is produced by changing the thickness of the liquid itself. Such an instrument is described in Section V-4-(d).

(2) The same law applies, at least theoretically, to the absorbing wedge—of liquid, glass, or gelatine. As usually used, such a wedge is moved past a narrow opening, such as the collimator slit, at right angles to the length of the slit. All such wedges, even the "neutral" ones, are more or less selective in their transmission as regards wave length. For this reason, as well as to check the theoretical variations of brightness, such wedges must be calibrated for spectrophotometric work.

(3) By changing the relative positions of two fine line gratings of the form used in making the cross-line screen (**22**) of the photo-engraver, the transmitted light may be made to vary continuously. Such a filter is practically non-selective.

(4) The transmission of a transparent plate will vary to some extent along a given external direction as the angle between the plate and the direction of the light is varied. This, of course, is because of the varying reflection.

(5) The brightness of a diffusing surface will vary as the angle between the incident light and the normal to the surface is changed. A good diffusing surface will obey the cosine law approximately.

(6) The illumination from a diffusing surface will vary with the effective area of the surface.

(7) When electric lamps are used, the brightness may be altered by varying the current through the lamp.

3. METHODS OF ILLUMINATION AND MEASUREMENT

Methods of illumination will usually vary with the use to which the instrument is to be put, also to some extent, perhaps, upon the type of instrument. It may be seen from Section V that certain types of instrument are especially adapted, because of the widely separated collimator slits, to the photometric comparison of different light sources, while others have been designed primarily for transmissive and reflective measurements where a single light source is desirable. With suitable auxiliary apparatus, however, any instrument may easily be adapted to any one of the three kinds of work.

Regardless of the instrument or the sort of measurements to be made, it is necessary for precise work that the illumination be such as to result in a photometric field of uniform brightness. It is also usually

desirable in spectrophotometry to make the illumination as great as possible under the given conditions.

A. Spectral Distribution of Relative Radiant Energy.—The spectral measurement of the relative radiant energy emitted by incandescent lamps or other sources in the visible is difficult or impossible by radiometric methods. High intensity, special apparatus, and experimental technique, are essential for such work. It has, therefore, been the usual custom, having measured radiometrically or otherwise obtained a source of known spectral distribution which may be used as a standard, to compare any unknown source spectrophotometrically with this standard, from which measurements its spectral distribution may be computed. Because of the sensibility of the eye the method is thus available for the relative measurement of sources of light—e.g., fluorescent spectra—for which radiometric methods may be far too insensitive.

This comparison of one source in terms of another should always be done by a *substitution method*—one of the few rules of spectrophotometry which may be considered standardized. In the substitution method the light from the standard source and the unknown source are made to traverse identical paths from the source to the eye, each being compared, in turn, with the light from a third source called the comparison source. Only in this way can selective absorption and reflection effects (which do not involve polarization) within the apparatus be certainly eliminated.

Uniform brightness of the photometric field is usually obtained by having the various sources illuminate diffusing surfaces, the light from which forms the photometric field. The diffusing surfaces must be perpendicular to the incident light if uniform brightness is to be secured, unless the distances or other conditions are such as to make this precaution unnecessary. Lenses may be used, if desirable, to increase the brightness, but in such a way that the image is sufficiently out of focus as to be uniform in brightness and of a size sufficient to fill the field. Chromatic effects should, of course, be avoided. It may be emphasized again that the standard and unknown sources must be treated identically.

Magnesium carbonate or oxide furnish probably the best diffusing surfaces. The light transmitted by ground glass or other diffusing screen may be used but, in general, is not as satisfactory as that reflected from the surfaces just mentioned. The selectivity of the diffusing surfaces should cause no trouble by the substitution method, but it may

be noted that ground glass is apt to be quite yellowish, the magnesia surfaces slightly so (**78**, p. 239).

Considerable increase of brightness may of course be secured if the source can be viewed directly or focussed upon the collimator slit, instead of the more usual method noted above. It has been previously mentioned that in this case polarization effects may need consideration. A study (**21**) of such effects has shown the variation of the polarization with the angle of emission, the constancy of this polarization with temperature and with wave length, and the small depolarizing action of ground glass. The polarization of the light from a straight tungsten filament in a direction normal to its length is about 12 per cent. (New data soon to be published indicate a value of about 20 per cent.) Since this polarization is independent of wave length, the relative spectral distribution of energy is not thereby affected but only the absolute magnitudes.

The brightness of electric lights is especially sensitive to small current or voltage changes. For the most precise work the lamps (comparison and either the standard or unknown) should be in separate storage battery circuits with auxiliary resistance and double potentiometer control. Fair results may also be obtained with voltmeter control and parallel connection on a single storage battery by constantly checking back to a given wave length.

B. Spectral Transmission.—In the relative energy measurements just described, one is limited largely as to what brightnesses can be used by the nature of the sources. Spectral energy distribution curves, however, do not as a rule vary rapidly with the wave length, and lack of brightness may accordingly partly be made up by an increase in the slit widths used. Spectral transmission curves, on the other hand, often vary extremely rapidly with wave length, and it is necessary for precise measurements upon a steep curve that very narrow slits be used. This necessitates high intensity in the light source.

As a rule, therefore, in spectral transmissive measurements the highest feasible illumination should be sought. This not only makes narrower slits possible of use but also will extend the measurements farther into the violet and red. Any of several obvious means may be used to cut down the brightness in the brighter parts of the spectrum if otherwise too high.

Several methods for obtaining high and uniform brightness are available. Sources like the acetylene flame and ribbon-filament lamp may be focused directly upon the slit. Troubles arising from imperfections (striae, bubbles, non-parallel surfaces, etc.) in the specimen being

tested will be less the closer to the slit it is placed. For optically perfect specimens two lenses may be used, so arranged that the light rays between them are parallel. The specimen is placed in this parallel beam. Its thickness will thus cause no change of focus. In either case undue heating of the sample should be prevented, as various glasses (**81**) and solutions are very susceptible to temperature change at certain wave lengths.

A second method is that in which the source illuminates diffusing surfaces of magnesia, ground glass, or other material as in the spectral energy measurements, the same care being taken to secure uniformity of illumination. The specimen is sometimes placed between the source of light and the diffusing surface. Unless necessary, however, this is not to be recommended, for the thickness of the specimen, changing the optical distance, causes a change in the illumination. The change in the optical distance is given by the formula (**125**, p. 55)

$$\Delta S = \frac{b(n-1)}{n},$$

where ΔS is the change in the optical distance, b is the thickness of the specimen, and n is the index of refraction.

It is very much better to place the specimen whose transmission is being measured between the diffusing surface and the slit of the spectrophotometer. Thick and imperfect specimens as well as lenses and optical instruments may thus be measured without error provided that the diffusing surface is uniformly bright and of sufficient extent to fill the photometric field, or the part of it being used, when the specimen is in the beam as well as when out.

The advantages of thus using an illuminated diffusing surface are well known. Very efficient ones may be obtained by inclosing incandescent lamps in a white lined box, the light being taken from the back interior wall through an opening in the front wall. The construction may be such as to give sufficient self ventilation, or an electric blower may be attached. An excellent diffusing surface is obtained by coating white enamel with magnesium oxide, and the whole interior of the box can be thus finished; or the light may be taken from an inserted block of magnesium carbonate, the rest of the interior being of any feasible finish. Several factors aid in giving high brightness, viz, total enclosed candle power, small distance between sources and reflecting surface, and high reflection and small area of enclosure walls.

Unless for some special reason light from the same source should be used to illuminate both parts of the field, as small fluctuations in the brightness will then be imperceptible and cause no errors in the measurement. This enables the lamps to be operated on an ordinary A.C. circuit, and unsteady sources like the mercury arc may be used without trouble.

The use of sources of homogeneous light such as the mercury arc or helium vacuum lamp is to be highly recommended as auxiliary to the heterogeneous light sources. They not only enable a constant check to be kept on the wave length calibration of the instrument but also are of great value when used for the actual transmissive measurements, especially for substances with rapidly varying absorption curves, since any error because of finite slit-widths is eliminated. The intense mercury blue and violet lines enable visual measurements to be accurately made at shorter wave lengths than with any other source.

(In the above discussion rectilinear (regular) transmission only has been considered (*Cf.* Sec. II-3). As in the case of reflection, certain types of transmission may be designated as diffuse or spread. But as previously noted, it has seemed best not to enter into a general discussion of diffusion. The subject is touched upon in the next section because it is the common case in reflection measurements. Much that is said there regarding the significance of the illumination applies also to diffuse transmission measurements.)

C. Spectral Reflection.—(a) Diffuse Reflection.—If all substances were perfectly diffusing, as that term has already been defined, the measurement of diffuse spectral reflection would be simplified. But all substances, even magnesium carbonate, are defective in this respect, and the various materials met with in practice exhibit all the varying degrees of diffusion between the approximately diffuse and the approximately specular.

For all substances, therefore, the amount of reflected light will vary with the nature and direction of the incident illumination. A complete specification of spectral reflection must for this reason have the method of illumination stated, and unless this method is a definite and reproducible one the reflection values are to a certain extent worthless.

A standard defining illumination for diffuse (or spread) reflection measurements ought, therefore, to be adopted. It is probable that the spherical or the hemispherical type of illumination should be used. Diffused light from the interior white wall is incident upon the sample (and upon the reference "white" sample) placed either upon the spher-

ical surface in the spherical design, or at the middle of the plane surface in the hemispherical design; for in these positions the illumination of the sample is equivalent in the two types. Measurements are then made through the opposite wall upon the light taken normally to the reflecting surface. The proper illumination may be obtained approximately by putting one or more strong lights within the inclosure, shielding the samples from the direct illumination; or the interior walls may be studded with a large number of miniature lamps uniformly distributed, the light from which may be allowed to fall directly upon the sample. This method will probably give the highest illumination consistent with the definition.

An important problem for settlement is the specification of a standard white diffusing surface for reference. Magnesium carbonate has usually been used and will perhaps prove one of the best available. Its total light reflectance is in the neighborhood of 98 per cent. Samples of the carbonate vary, however, not only in total reflectance but also in selectivity. That so far examined has proved slightly yellowish (**78**, p.239). Magnesium oxide has been found to vary from yellow through white to blue depending upon the thickness of the reflecting layer (**122**, p. 379). It is possible that a reproducible white, unselective and of known reflectance (if not 100 per cent), could be obtained from the oxide deposited upon magnesium carbonate or other suitable white back-ground. This is an interesting problem for research, and very important from the standpoint of color specification.

(b) Specular Reflection.—This can be measured relative to that of some surface taken as a standard, whose reflectance is known, or it may be obtained without reference to any other material. In either case the angle of reflection (equaling the angle of incidence) should be stated as part of the data, since the reflectance will vary with this angle.

For the measurement of relative reflectance, using a "standard," it is merely necessary to reflect light from some source on to a diffusing surface which forms the basis of the photometric field, the reflecting surfaces being first the standard and then the unknown sample. Or the two samples may in turn reflect the light from a source or an illuminated diffusing surface directly into the instrument.

For absolute reflectance a diffusing surface may be illuminated first by a source alone and then by the source reflected from the specimen, the direct light being cut off. For this purpose the mirror and light source should be mounted in such a way that the distance from the

source to the diffusing surface is the same either by the direct route or by the reflecting route and that the angle of incidence of the light on the diffusing surface is the same in both cases.

As in the case of spectral energy or transmissive measurements the highest brightness will be obtained by focussing the light source directly on the slit. Specular reflectance has been recently measured (**30**) that way, an image of the source without reflection and an image as reflected by the sample being focussed successively on the collimator slit. The method as used permits of the measurement of reflectance for curved as well as plane surfaces, for small surfaces, and for those with superficial irregularities.

4. SENSIBILITY—PRECISION—ACCURACY

A. The Photometric Field.—One of the most important factors in securing high precision of measurement is the fineness of the dividing line separating the two parts of the photometric field, Fig. 6. It should disappear when a match has been obtained. This applies to what is known as the simple comparison field. It is not so essential in the case of the contrast field, type *II-d*, whose sensibility is at a maximum for a contrast of about 3½ per cent.

A field brightness of 2.5 millilamberts (for full pupil illumination) and a diameter of 2° have been proposed (**24**) as the essential conditions for bringing into agreement heterochromatic measurements made by the two ordinary kinds of photometry—viz, the so-called equality-of-brightness (simultaneous comparison) and flicker (alternate comparison) methods. While the original data on which these values were based were, perhaps, rather meager, yet all the evidence available points to their approximate correctness. In spectrophotometry, i.e., homochromatic photometry, however, it is of far less importance than in heterochromatic photometry that the field size and brightness be of the values stated. If the two parts of the field are identical in chroma, these two factors should have no influence on the accuracy of results, provided measurements are made under conditions of good precision. If for one reason or another, the two parts of the field do differ much in chroma (unusual in spectrophotometry), then to that extent it is of importance to keep somewhere near the values stated.

From the standpoint of precision alone a field size intermediate between 1° and 10° will be found satisfactory. Probably all spectrophotometers have fields within this range. A brightness of 2.5 millilamberts with full pupil illumination is equal to approximately

25 or 50 millilamberts viewed through a 1-mm.^{2} slit. Even for heterochromatic photometry brightnesses greater than these probably do not introduce error. In spectrophotometry, therefore, one should strive for the maximum feasible illumination, so that the field brightnesses even after the dispersion will yet be of sufficient magnitude. One need not worry about their being too bright. As previously noted, narrowing the slits will not only remedy this but will also increase the purity of the spectral region, and the greater the brightness the farther into the red and violet can measurements be made. Unlike heterochromatic measurements, low brightnesses do not, in general, cause errors in spectrophotometry except those resulting from lowered precision. One is, therefore, limited only by his own ability, and it will be found that measurements can be made at brightnesses so low that but little sense of hue remains.

B. The Photometric Scale.—Another factor of considerable importance in attaining high precision in all photometric work is the ease with which the brightness variations can be effected. The adjustment —of the distance, angle of the nicol, sector opening, etc.— should be smooth, not jerky, enabling one to adjust rapidly back and forth on either side of the correct position. Lost motion in any part is very undesirable. If present, it must be carefully guarded against.

Another essential factor is the proper division of the scale by which the brightness variations are read and from which the various quantities are computed. In general, the scale should be so divided that 0.1 per cent of the range of variation being used can be easily read. For example, the range of many scales is from 0 to 90 or 100 and it should be possible on such scales to read to 1/10 of a division. If a variable distance scale is used over a range of one or two meters, it may be sufficient to read to the nearest millimeter. The ideal is to have the smallest scale division about equivalent to the photometric precision of the eye. In addition to such a study, the best part of the scale in which to work should be determined, i.e., that part in which the change of brightness per division is the least.

C. Comfort of the Observer.—It may seem almost unnecessary to note that the comfort of the observer is very essential to the best photometry. Even more obvious is the necessity of excluding all extraneous light from the eye. This is of great importance where the field brightness is very low, as in the end regions of the spectrum. An eye shield should be made, blackened on the inside, which is both comfortable

and effective. The individual can quickly decide by actual trial if this is the case.

D. Precision and Accuracy.—The best photometric precision, expressed in terms of average deviation of a single observation from the mean, is of the order of magnitude of 0.3 per cent (**25**). This can be reached with the contrast field, type *II-d*, Fig. 6, or with the simple comparison field under the best conditions. It is largely independent of the brightness over a considerable range, including the brightnesses ordinarily used in photometric work.

This precision should be nearly reached, if not quite, with the spectrophotometer in the brighter regions of the spectrum. It will, of course, decrease for very low brightnesses, necessarily as the end regions of the visible spectrum are approached.

The distinction between precision and accuracy should be kept clearly in mind in the study of the spectrophotometer. After determining if the apparatus has been assembled and adjusted so as to attain satisfactory precision of readings, it is very important to test the accuracy of the results obtained from these readings. High precision and low accuracy may easily go together.

If the instrument is one not already dependent upon the variable sector, the fixed sector is an excellent means of testing the accuracy of the method used for brightness variation. The fixed aperture sector may be itself calibrated mechanically to an accuracy better than the photometric precision. The inverse square law may also be made the basis for such checking.

The reliability of the photometric device is not sufficient, however, to insure accuracy in all cases on the spectrophotometer. In the end regions of the spectrum, for example, stray light may cause errors in the final results undetected by the above methods of checking. The magnitude of such errors may vary largely with the kind of measurements being made. If all experimental conditions are not perfect, the possible errors will likely be smaller if the spectral distribution of radiant energy of one lamp is being measured relative to a similar lamp or if the transmission of a neutral glass is being determined, than if two sources are being compared widely different in spectral distribution or if a glass is being measured whose transmission varies rapidly throughout the spectrum.

Any of several methods are valuable in a study of such possible errors. If another visual instrument is available, or better yet one of the methods described in Section VI, whose spectral sensitivity improves as

the visual decreases, an entirely independent set of measurements of the same function will serve as a valuable inter-check of both methods. If the values do not agree, the cause may be studied. If they do agree, the data are in all probability reliable. Another method, if standard lamps, glasses, etc., are available whose spectral data are accurately known, is to use such standards for a test of the instrument. The transmissions of different thicknesses of a given solution will, on the basis of Lambert's law, assist in such a study.

Whatever the method, too much importance cannot be attached to this study of accuracy. Only those who have had the opportunity of working with several different methods are apt to realize the large errors that may be present in "smooth" spectral curves obtained by a single method.

Of the factors affecting accuracy present with practically all instruments, stray light has, perhaps, been sufficiently discussed. It may be added, however, that when using filters for its elimination, error may be introduced instead of eliminated if it is attempted to use the filter at wave lengths where its transmission is very low.

Error may also arise from neglect of the fact that with a heterogeneous source there is always included by a slit of finite width a small range of wave lengths on either side of that at which the setting is nominally made. The successive overlapping of the various spectral images of each part of the collimator slit result in what is called an impure spectrum. The wider the collimator slit the greater the impurity and the wider the ocular slit the greater is the wave length range of the impure spectrum entering the eye. The equations by which a result obtained experimentally with the finite slit widths and impure spectrum can be corrected to the true result for the pure spectrum have been worked out by Merritt (**75**) and by Hyde (**78**), the former as a function of wave length for a prism instrument, the latter as a function of deviation angle for a prism instrument (equivalent to wave length for a grating instrument). The major part of the correction arises from the second derivative of the luminosity curve at the ocular slit. It will be eliminated if two sources are being compared whose spectral distributions of radiant energy bear a constant ratio to each other, or if the transmission or reflection of non-selective media are being measured. It becomes extreme at the maxima or minima of narrow absorption bands.

There are two experimental methods of reducing this correction. The use of homogeneous light eliminates it under all conditions. The

use of narrow slits with the heterogeneous source will often practically eliminate it. For a given sum of collimator plus ocular slit widths, the correction is least if they are equal. For all but the more extreme cases slits of 0.10 or 0.20 mm on the usual prism instrument will reduce such corrections to negligible amounts (*Cf.* Fig. 3).

In transmission measurements the changes resulting from changes in temperature have already been noted. Certain glasses, crystals, inorganic solutions and probably many other materials, show rapid changes with temperature.

5. THE DISAPPEARING FILAMENT OPTICAL PYROMETER

The disappearing filament optical pyrometer (often called the Morse or the Holborn-Kurlbaum pyrometer) finds a particular application in the study of spectral characteristics of small objects or light sources.

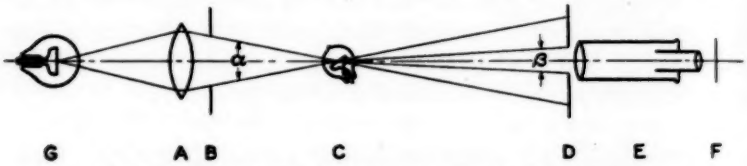

FIG. 7.—*Essential parts of a disappearing-filament optical pyrometer.*

A—Object glass. B—Entrance-cone diaphragm. C—Pyrometer filament. D—Exit-cone diaphragm. E—Eye-piece. F—Glass pyrometer filter. G—Light source under investigation. (The parts A, B, C, D, E and F constitute the optical pyrometer.)

Its operation is based on the fact that an incandescent filament, as seen through certain colored filters, may be made to disappear against the image of a bright object or light source formed in the plane of the filament. A diagram of the essential parts of an instrument is shown in Fig. 7. In some instruments approximately homogeneous light is obtained by using dispersing systems instead of colored filters.

In general, in the disappearing filament optical pyrometer, the filament and image are not of the same brightness when disappearance occurs. For this reason, certain precautions, more or less peculiar to this instrument, must be observed in order that the relative brightnesses of filament and image at disappearance may be constant (**36, 37**). For accuracy, there should be axial symmetry, as far as possible, of the optical parts; the part of the pyrometer filament used should be in this axis; the entrance cone angle α must be larger than the exit cone angle β; excepting possibly under certain special conditions, angles α and β should be kept constant during a single comparison; the optical system

should be such as to eliminate the disturbing effects of diffraction in case diffraction occurs.

To calibrate a pyrometer with a given colored pyrometer filter, it is necessary to determine the relation between the brightness of a light source at which the pyrometer is sighted and the current through the pyrometer filament at disappearance. A set of calibrated rotating sectored disks placed between G and C and close to the one or the other is most convenient for this purpose. Just how these calibration curves, showing relative brightnesses as functions of the pyrometer currents for the various filters, may be used in studying the spectral characteristics of emitted, transmitted, or reflected light is more or less evident.

Since all pyrometer filters transmit a considerable range of wave lengths, results obtained with them are subject to certain limitations. For radiant energy having spectral distributions in the visible relatively the same as for a black body, effective wave lengths have been defined (**38, 39**). From their consideration, it is possible to assign results obtained to strictly definite wave lengths (**40, 41**).

In case the light from the source being studied is polarized, a small error may result from the application of calibration curves obtained with unpolarized light (**36**).

6. THE FLICKER PHOTOMETER

Because the flicker photometer is occasionally made a part of spectrophotometric apparatus it seems proper to refer to it briefly in this section. The two methods of photometry and the experimental conditions under which they give agreement have been noted in section 4 above.

For lights of the same chroma, the equality-of-brightness method is undoubtedly superior in precision to the flicker method. The average deviation of a single observation from the mean in the case of the latter is of the order of magnitude of 0.75 per cent (**25**) as against 0.3 per cent for the former under the best conditions. With increasing chroma difference in the two halves of the field, however, the equality-of-brightness method rapidly loses precision, and soon becomes an impossible method for most observers, so far as any precision is concerned. On the other hand, the precision by the flicker method is largely unaffected by differences of chroma. Even for chroma differences as small as that between the carbon lamp and the gas-filled tungsten lamp, the flicker method is superior to the other.

Flicker photometry not being universally accepted as the equivalent of equality-of-brightness photometry has, in certain cases, led to the use of what is called the step-by-step, or cascade, method, whereby lights of large chroma difference may be photometered by the successive measurement of the smaller chroma differences into which the large difference may be divided. It has proved a reliable method for certain investigations, notably the measurement of the visibility of radiant energy (**34**: **35**).

V. VISUAL INSTRUMENTS

1. EARLY ATTEMPTS AT SPECTROPHOTOMETRY

Early in the nineteenth century Fraunhofer (**42**) tried to measure the relative intensity in the sun's spectrum—by a method, however, quite imperfect. If heterogeneous light is mixed with spectral light and the intensity of the former is increased, the appearance of hue will eventually disappear. From the known intensities of the heterogeneous light when the hue became imperceptible, a measure of the relative intensities of the spectral light was taken. The idea was later tried by Vierordt (**42**) and by Draper (**42**) the latter of whom came to the remarkable but erroneous conclusion that for a normal spectrum (from a grating) "the luminous intensity is equal in all the visible regions."

Govi (**43**) was apparently the first to use what might be called a spectrophotometer. He projected two spectra, each from a different source and dispersed by the same prism, on to a white diffusing surface. These contiguous spectra were then examined through a diaphragm by which any small region could be selected at will. Brightnesses were varied by changing the distances of the light sources. He also realized the possibilities in the use of polarization methods for varying the brightness.

Vierordt, after trying Fraunhofer's method as noted above, developed a quantitative method (**44**) which formed the basis of several spectrophotometers developed and used by later investigators. He is called by Kayser "der Vater der Quantitativen Spectralanalyse durch Absorption." These instruments are described in the next section.

2. JUXTAPOSED-SPECTRA INSTRUMENTS

It was noted in Section III-2 that the spectral image of the collimator slit, formed in the plane of the ocular slit, transmitted by it, and viewed through an eyepiece, could become the basis of a photometric field; that is, if the slits are not too wide, the rectangular area of the spectrum

transmitted by the ocular slit (or a diaphragm) will comprise a field of uniform hue, and if means are available for properly dividing this field and varying the brightness of its parts the instrument becomes a spectrophotometer.

In devising such an instrument, Vierordt (**44**) replaced the usual collimator slit with a divided slit, the width of each part of which was independently controlled by a separate micrometer. This resulted in the formation of two spectra, one directly above the other, which could be seen through the eyepiece. A suitable diaphragm screened off all parts of the spectra except those being compared, giving a field of type *I*, Fig. 6. The brightness in either half of the field could be varied by the observer to obtain a photometric match by merely varying the width of the respective part of the collimator slit.

This had all the essential elements of the spectrophotometer, and could be used to measure relative spectral energy distribution, transmission, or reflection. There were, however, two serious faults in the original instrument—one, that unilateral slits were used, and another in the fact that, because of the small separation of the collimator slits, the two spectra were separated by a small dark space sufficient to decidedly reduce the precision.

Improvements, therefore, consisted in replacing the unilateral slits with bilateral ones, in replacing the variable slit width method of varying brightness by other methods, and in devising means for eliminating the space between the two spectra. Bilateral slits were adopted by Krüss (**50**) and by most later investigators, not only on this type of instrument but on all spectrophotometers.

Polarization methods of varying the brightness have been used by Glan, Crova, Hüfner, Nutting, and others. These are described below. Nichols (**59**) used the variable distance method, placing the spectrometer on a photometer bar and moving it back and forth between two stationary light sources for the photometric match. He was probably the first to use a grating dispersing system in spectrophotometry. Variable sectors or other means may, of course, also be used to vary the brightness.

Several methods have been used to bring the light into the two halves of the collimator slit in the proper juxtaposition, resulting in two spectra separated only by a very fine line. In most cases these devices have also had the desirable feature of enabling the two beams of light to be kept more or less separated before entering the collimator slit. Such have been the rhomb used by Hüfner (**55**) and others, and the simple or

compound total reflection prism used by Vierordt, Nichols, Bell (72), Nutting, and others, these devices being often equivalent to Lummer-Brodhun cubes. Split collimator lenses (56) have also been used for juxtaposing the two spectra.

The juxtaposed-spectra type of instrument has the desirable feature that the only errors caused by stray light will be those resulting from loss of sensibility. The optical arrangement is such that the stray light present will under all circumstances be scattered equally over the two spectra comprising the two parts of the photometric field. This is not the case with some of the monochromatic-field instruments described below. This juxtaposed-spectra method has, however, the undesirable feature that, either because of varying hue or varying brightness (as when measuring the transmission of many glasses), which would otherwise cause a nonuniform field, the ocular slit or diaphragm has to be narrowed to the point of interfering with the photometric precision. The dividing line between the spectra also cannot be made to disappear as completely as is possible in the monochromatic-field spectrophotometers.

3. POLARIZATION METHODS

A. The Juxtaposed-Spectra Type.—It was noted above that polarizing devices were early adopted as a means of varying the brightness of one or both contiguous spectra forming the basis of the photometric field in the juxtaposed-spectra instrument.

Perhaps the first one to do this was Glan (45) who used a method similar in many respects to the König-Martens spectrophotometer described in detail below. By means of a rochon prism within the instrument, he obtained two beams of light, polarized mutually at right angles, which, after passage through a nicol prism, formed the two contiguous spectra. Rotation of the nicol, would, in general, increase the brightness of one part of the field while decreasing it in the other, the $\tan^2$ relation holding as in the König-Martens instrument.

In Glazebrook's spectrophotometer (51) two beams at right angles to each other were each polarized by a nicol in a mutually perpendicular plane, and finally brought to form two contiguous spectra which were viewed through a third nicol. Rotation of this third nicol varied the brightness as in the Glan instrument.

In Crova's instrument (52) the light in one half the field only is polarized. This is accomplished by means of two nicol prisms in series. One is rotated and the brightness varies as the $\sin^2$ of the angle, as in

the Brace-Lemon spectrophotometer described below. Zenker (**54**) used three nicols in series, rotating the middle one and using the $\sin^4$ relation.

In Hüfner's spectrophotometer (**46**; **55**) the same relation is used, but the nicols are separated, one being placed before part of the collimator slit so as to polarize one beam, the other in the telescope. While both beams pass through the latter nicol, its rotation will change the brightness only in the beam already polarized. The polarizing actions of the rhomb and dispersing prism were made to neutralize each other by making them of the same kind of glass and of the proper angles.

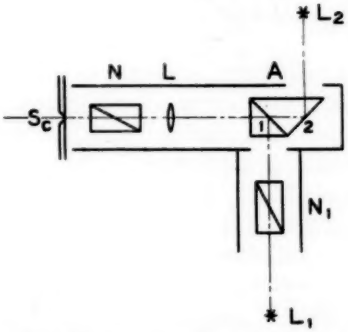

FIG. 8.—*Original design of Nutting polarization photometer.*

S_c—Collimator slit of spectrometer. N, N_1—Nicol prisms. L—Lens. A (1, 2)—Total reflection prisms, alternately silvered and clear on common face, giving photometric field of type I, Fig. 6.

Twyman (**69**) studied the errors liable to be present in polarization instruments as a result of the polarizing action of the dispersing prism, rediscovering the complete neutralizing action of the Hüfner rhomb if properly made. Houstoun (**70**) used a complex rhomb, a combination of glass and calcite, which polarizes both beams in planes at right angles to each other. Rotation of the ocular nicol varies the brightness on the $\tan^2$ basis as in the Glan or König-Martens spectrophotometers.

The $\sin^2$ relation also holds in Nutting's pocket spectrophotometer (**68**), in which one beam is polarized externally as in the Hüfner instrument, while the rotating nicol, transmitting both beams, is placed just inside the collimator slit. Nutting, (**77**) has also devised a polarization photometer, complete in itself, which may be used with the Hilger (**91**) or Gaertner (**94**) spectrometers. The original design is shown in Fig. 8. The common surface of prisms 1 and 2 is alternately silvered and clear. A real image of these strips (illuminated respectively by

L_1 and L_2) is formed in the plane of S_c by means of the lens L. Brightness variation was secured by the rotation of nicol N_1. In the improved designs as used by Gaertner and Hilger, nicol N is rotated instead of N_1, and for the purpose of facilitating transmissive measurements the optical arrangement is such that both beams arise from a single source placed along the collimator axis (extended), as in some of the instruments illustrated below (Figs. 9, 12).

Bausch and Lomb (**93**) have likewise adapted their Martens photometer for use with their spectrometer. The essential parts and action of the Martens photometer are similar to those illustrated in the König-Martens spectrophotometer (Fig. 9) except, of course, that there is no dispersing prism.

B. The Monochromatic-Field Type.—In the instruments so far described, the spectral field will be monochromatic only if the ocular slit width is made less than the hue limen, the smallest wave length interval just perceptible as a difference in hue. If, on the other hand, the eyepiece is removed and the eye is placed at the ocular slit, the field seen will be uniform in chroma for all slit widths that are otherwise feasible. The homogeneity of the light will vary with the slit widths but the color will be monochromatic. Furthermore, its uniformity will be practically unaffected by the spectral gradient of the luminosity. In this type of instrument the division of the field must be secured at some place other than at the collimator slit. It is usually effected between the collimator and telescope objectives, as noted in the various instruments described below.

Apparently the first to use the monochromatic-field spectrophotometer was Gouy (**48**), in connection with his study of colored flames. He added a second collimator to his two-prism, minimum-deviation spectrometer, placing it approximately at right angles to the first collimator. A mirror properly placed at the intersection of the two collimator axes obstructed part of the light from the first collimator replacing it with light from the second so that a field of Type *II-a*, Fig. 6, resulted, with horizontal dividing line. Brightness was varied by rotating one of a pair of nicols placed in the second collimator, as in the Brace-Lemon spectrophotometer described below.

This instrument, the first of its kind, was as complete in concept as was Vierordt's juxtaposed-spectra instrument, but like his undoubtedly lacked the precision of later instruments, in which better optical means were devised for securing the divided field. The first of these monochromatic field instruments of high precision which employed polariza-

tion methods of varying the brightness has come to be known as the König-Martens spectrophotometer. Another is the Brace-Lemon instrument. These are described below. A recent addition to this class of instrument is the combination photometer, spectrophotometer, and polarimeter designed by Yvon (**85**).

(*a*) *The König-Martens Spectrophotometer* (**60**; **62**; **66**).—An outline plan of the instrument is shown in Fig. 9. The collimator and telescope lie in a vertical plane with the refracting edge of the dispersing prism horizontal—the opposite of most spectrophotometers. The telescope pointing upward at an angle makes a very convenient position for the observer.

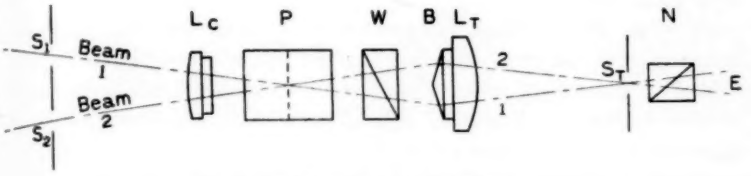

FIG. 9.—*König-Martens spectrophotometer.*

S_1, S_2—Separate parts of single collimator slit. Slit length is in plane of paper. L_c—Collimator lens. P—Dispersing prism. The deviation is away from the plane of the paper. W—Wollaston prism. I_c—Telescope lens. S_c—Ocular slit. N—Nicol prism. E—Position of the eye. B—Biprism, giving photometric field of type II-a, Fig. 6.

The light from beams 1 and 2 traverses the instrument as shown. By means of the wollaston prism each beam is split into two parts vibrating at right angles to each other. One part of each beam is lost within the instrument; the remaining parts, polarized mutually perpendicular, are brought by means of the biprism and telescope lens to form the two halves of the photometric field, which is viewed by the eye through the nicol prism. The field is of type *II-a*, Fig. 6, the dividing line being produced by the apex of the biprism.

Since the two beams of light reaching the nicol are polarized at right angles to each other, a rotation of the nicol will increase the brightness of one half of the field while decreasing that of the other half, one becoming a maximum when the other becomes extinct, and vice versa. The angular scale is made to read zero for one of the positions of extinction.

If one of the original beams, e.g., beam 1, is kept constant while the other, beam 2, is varied, and a photometric match has been obtained in two different cases, the brightness of beam 2 in the first case to that in the second case will be given by the ratio of the squares of the tan-

gents (or cotangents) of the angles of match. If beams 1 and 2 may be interchanged, the ratio of brightness is the product of the tangent of the angle of match in one case by the cotangent in the other.

This interchange of beams 1 and 2 is the usual procedure in transmissive and reflective measurements, for which this spectrophotometer is primarily adapted. An illumination similar to that illustrated in Fig. 12 may be used. With simple auxiliary apparatus, however, the measurement of relative spectral radiant energy is easily made, and the instrument has been used (**83**) in the study of the spectral distribution of fluctuating sources such as the high powered arc light. A recent study (**96**) has been made of the accuracy and precision attainable with this instrument.

(*b*) *The Brace-Lemon Spectrophotometer.*—The original Brace instrument (**63**) followed the Lummer-Brodhun spectrophotometer (see below) in the use of two collimators, but the photometric field was formed within the dispersing prism itself. Conservation of light is thus at a maximum. The prism P (Fig. 10) consists of two 30° prisms cemented together, as shown, with α-monobromonapthalene. As this has practically the same refractive index as the glass used, internal reflections are largely eliminated. On part 2 of this compound prism a narrow silver strip has been deposited extending from base to apex midway from top to bottom. Above and below this strip, light from S_1 reaches S_t as in the ordinary spectrometer. The strip itself will obstruct the light from S_1 and reflect that from S_2, so that the eye placed at S_t will see a field of type *II-b*, Fig. 6. Methods of securing the proper adjustments of this instrument are noted by Tuckerman (**65**).

No means of varying the brightness was provided on the original instrument except the variable slit-width method. This having been proved a more or less inaccurate method, Lemon (**80**) added a pair of nicols to the instrument, inserting them in C_2 as shown. To avoid error from the polarizing action of the dispersing prism, nicol N' must be kept stationary. Variation of brightness is secured by rotating N and this brightness will be proportional to the square of the sine of the angle of rotation measured from the position of extinction.

The instrument is especially well adapted to the measurement of the relative energy distribution of light sources. In this case the standard and unknown should in turn illuminate slit S_1 and the comparison lamp S_2. Such measurements, as well as transmissive and reflective measurements, may be carried out as described in Section IV-3.

4. NON-POLARIZATION MONOCHROMATIC-FIELD INSTRUMENTS

(*a*) *The Lummer-Brodhun Spectrophotometer.*—The first monochromatic-field instrument of high precision was the Lummer-Brodhun spectrophotometer (**58**) this antedating the Brace and final König-Martens instruments by about ten years. The essential details are shown in Fig. 11. The crux of the instrument is the Lummer-Brodhun cube *L-B*. This, in its simplest form, consists of two pieces of glass brought into

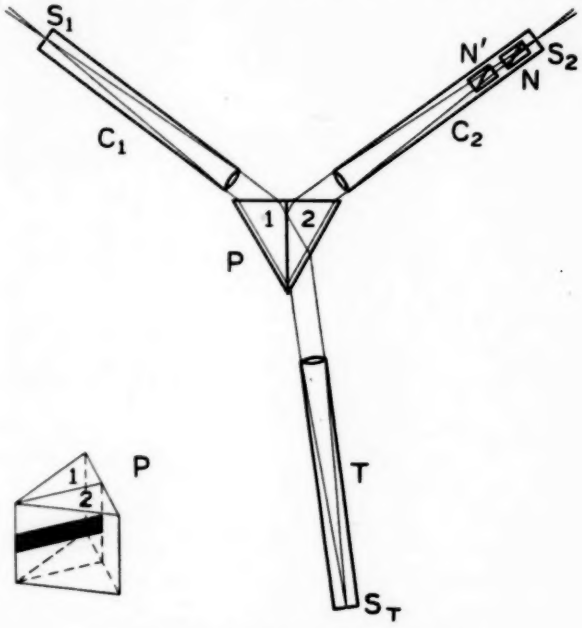

FIG. 10.—*Brace-Lemon spectrophotometer.*

S_1, S_2—Collimator slits. N, N'—Nicol prisms. S_T—Ocular slit. P—Brace double prism, giving photometric field of type II-b, Fig. 6.

optical contact. As illustrated, part 2 is a right angled prism, which if used alone would reflect all of the light from S_2 towards P. A small part of the surface of part 1 is, however, forced against part 2, the rest of that surface of part 1 being ground away so as not to be in contact with part 2. When the eye is placed at S_t, it will, therefore, see a field of type *II-c*, Fig. 6, wherein the light in part 1 of that field will have come from S_1 and that in part 2 from S_2. Other forms of simple comparison cubes are used.

In still a different type of cube a field of type *II-d*, Fig. 6, results. By the use of clear glass plates suitably placed before the cube, the trapezoidal parts of the field suffer an 8 per cent decrease in brightness, and the photometric match is obtained by so altering the brightness as to make the darker trapezoidal portions show equal contrast with the surrounding field. Hyde and Cady (**27**) have devised a method of decreasing the contrast from 8 per cent to 3½ per cent, increasing the precision somewhat. As already noted, the precision of the contrast field is the equal, if not the superior, of any type which has been devised.

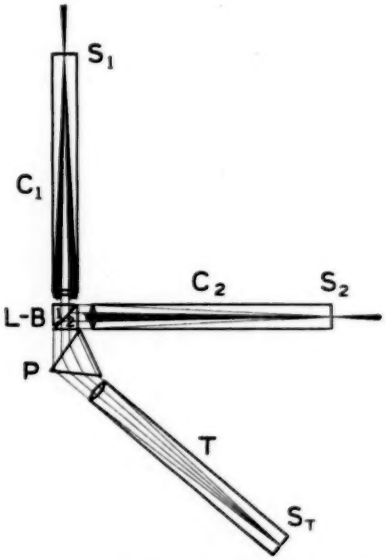

FIG. 11.—*Lummer-Brodhun spectrophotometer.*

S_1, S_2—Collimator slits. S_T—Ocular slit. Shaded parts of beams not used. L-B—Lummer-Brodhun cube, giving field of type II-c, Fig. 6. Other L-B cubes give field of type II-d, contrast form.

The Lummer-Brodhun spectrophotometer, like the Brace, is well adapted for the measurement of relative spectral radiant energy, and has been widely used for this purpose. Any of the various methods mentioned in Section IV-2 may be adapted for brightness variation with this instrument.

(*b*) *The Keuffel and Esser Color Analyser* (**92**).—This instrument is characterized by its direct-reading features. It is designed for the spectrophotometric measurement of the transmissive and reflective

properties of materials. Not only may wave length be read directly on the drum which rotates the prism (a characteristic of constant deviation spectrometers), but also the transmission or reflection of the material being tested is read directly at each photometric setting.

This is made possible by means of the special variable sector used for brightness variation. With it the relative intensities of the two beams can be varied from 0 to 110 per cent and the scale reads accordingly. For low values of transmission or reflection a certain device quadruples the precision of reading.

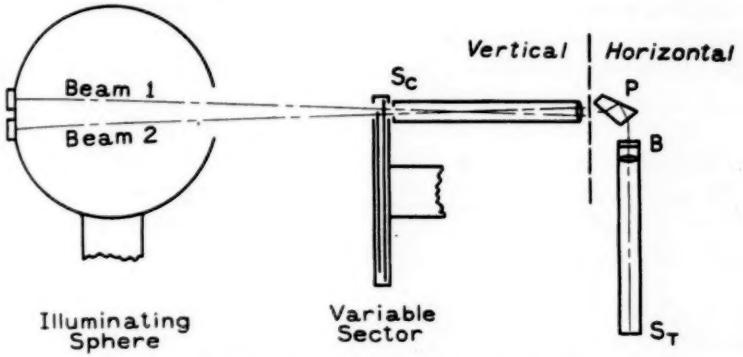

FIG. 12.—*Keuffel & Esser color analyser.*

B—Biprism, giving field of type II-a, Fig. 6, with horizontal dividing line. S_c—Collimator slit. S_T—Ocular slit. (The illuminating sphere, variable sector, and spectrometer are rigidly mounted on one base, insuring permanent adjustment.)

The arrangement of the apparatus is outlined in Fig. 12. The photometric field, of type *II-a*, Fig. 6 (dividing line horizontal), is formed by the biprism *B* placed over the telescope lens. By means of this biprism the light in one half the field comes from the lower part of the collimator slit, having passed through the variable sector, the light in the other half comes from the upper part of the slit after passing through the constant sector.

For transmissive measurements the two beams of light originate from two pieces of magnesium carbonate in the illuminating sphere and the sample is placed in beam 1 between the sphere and sector. For reflective measurements the sample being tested replaces the carbonate for this beam.

The necessary condition for accurate measurement is that a photometric match shall be obtained at all wave lengths when the sector is

set at 100.0 and the two beams originate from two similar pieces of carbonate.

(*c*) *Ives' Symmetrical Instrument.*—The study of scattered light in spectrophotometry made by Ives has already been noted. The method finally used by him (**74**) had the advantage of the large monochromatic field with its high precision, while the scattered light was distributed equally over both parts of the field as in the juxtaposed-spectra instruments.

This was accomplished by placing the optical parts which delineate the photometric field external to the collimator slit of the spectrometer instead of between the collimator and telescope lenses as is usually done in the monochromatic-field type. Fig. 13 illustrates this. Quoting

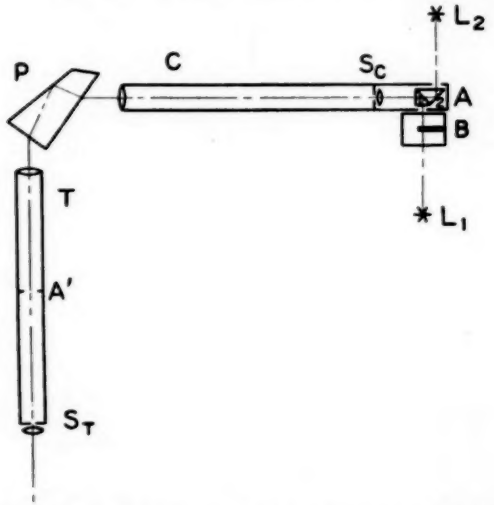

FIG. 13.—*Ives' method of securing monochromatic field with stray light symmetry.*

A—Optical device giving at A' a photometric field of type II-b, Fig. 6. B—Brodhun variable sector. (See Sec. V-4 (c) for further description.)

from the original paper (with changed symbols): "At A is placed any convenient device for forming a divided photometric field, . . . L_1 and L_2 are the two sources to be compared, which must be extended, preferably white surfaces illuminated by the lights compared. At S_c (the slit) is a convex lens, where distance and focal length are such that it forms, with the collimator and telescope lenses, an image of the prism face 1 at some place in the telescope tube A', as distant as possible

from the lenses and prism of the instrument. B is a Brodhun sector disc for reducing the intensity of one source by a measurable amount. At S_1 is a spectacle lens to focus the image at A'." Other details are given by the author.

The complete symmetry of both beams within the instrument is the essential condition for eliminating inaccuracies from scattered light. Not only do Ives' method and the juxtaposed-spectra instruments accomplish this, but also the König-Martens and Keuffel-Esser spectrophotometers should be nearly free from this defect. It should be most pronounced in instruments like the Lummer-Brodhun and Brace spectrophotometers. However, as previously noted, proper filters furnish sufficient protection against this trouble, and because of the increased precision should always be used, even with the symmetrical instruments.

Thovert's spectrophotometer (**73**), similar to Ives' construction, is described by the author as a convenient means of altering an ordinary spectroscope to a spectrophotometer and dispensing with the double collimator of the Lummer-Brodhun instrument while obtaining a similar field.

(*d*) *Priest's Exponential Spectrophotometer.*—A variation-of-thickness photometer has recently been designed by Priest (**84**) for the direct-reading measurement of the transmissive constants of liquids. The following are the essential features:

Two beams of light proceed horizontally, one above the other, from a uniformly illuminated vertical surface. A rotating sector of known transmission is interposed in the upper beam.

By means of two totally reflecting, partially immersed rhombs, the lower beam is diverted through a variable thickness of liquid determined by the distance between the rhombs, one of which is carried by a slide on a track parallel to the beams of light. The liquid is contained in a horizontal trough with open top into which the rhombs dip.

The two beams are brought into juxtaposition in the photometric field by means of an arrangement of biprisms. The thickness of the liquid in the lower beam is varied until its transmittance equals the transmission of the sectored disc. A suitable scale provides for the direct reading of transmissivity or the logarithm of transmissivity.

Light of definite wave length may be obtained either by (a) the use of light filters with a selective source, such as the mercury arc, or (b) dispersion with a prism which converts the instrument literally into a spectrophotometer.

(*e*) *Other Spectrophotometers of this Type.—The Brace spectrophotometer* (**63**) has already been sufficiently described in connection with Lemon's modification.

The Shook differential spectrophotometer (**82**) in which the two collimator slits are controlled by a single micrometer, the sum of their slit-widths remaining constant, seems to be a step in the wrong direction since the unilateral slit width method is the basis of brightness variation.

Bull's spectrophotometer (**86**) is unique in its method of brightness variation. In this instrument the ocular slit is divided into halves, and brightness variation effected by varying the length of one half the ocular slit. For this and the various other instruments so briefly noted, reference should be made to the original papers for the various details.

5. OTHER METHODS

By placing a rod in the path of two sets of rays, Abney (**118**) cast two shadows upon a screen, causing them to touch one another. By varying the brightness in one beam with his variable rotating sector, he could equalize the brightness of the two shadows and thus obtain photometric readings.

Milne (**79**) used the flicker principle in his spectrophotometer, after previously using the juxtaposed-spectra type of instrument.

The action of a complicated polarization instrument by Wild (**53**) depends upon the vanishing of the interference bands formed by the proper superposition of two beams of light from any given source.

Still another method is used by Pulfrich (**88**) in whose instrument a stereoscopic effect is the basis of the criterion for equality of brightness.

None of these methods has the precision of the usual equality-of-brightness methods previously described for ordinary spectrophotometry; but, as noted in Section IV-6, the flicker method is of immediate value for the comparison of lights differing in chroma.

6. INSTRUMENTS AT PRESENT AVAILABLE

Of the juxtaposed-spectra instruments there are available commercially:—the Hüfner spectrophotometer, sold by Hilger,[6] the Nutting photometer with spectrometer sold by Hilger in England and Gaertner[7] in this country, and the Martens photometer with spectrometer sold by Bausch and Lomb.[8] As advertised, these have been developed

[6] Adam Hilger, Ltd., 75a Camden Road, London.
[7] The Gaertner Scientific Corp., 1201 Wrightwood Ave., Chicago, Ill.
[8] Bausch and Lomb Opt. Co., Rochester, N. Y.

primarily for transmissive measurements. The complete equipment includes in all cases the spectrometer with polarization photometric attachments as already noted, a source of light separated optically into two parallel beams, and tubes with support for containing solutions. With suitable illumination, as described in Section IV-3-C and as illustrated with the K and E color analyzer, Fig. 12, the apparatus could also be used for reflection measurements.

Several monochromatic-field instruments are in use in this country. The König-Martens, Lummer-Brodhun, and other spectrophotometers were made by Schmidt and Haensch[9] before the war. Their availability from that source has since been somewhat uncertain, but it is now understood that they can again be obtained either from the makers or from importers in this country. The Brace-Lemon spectrophotometer has been advertised by Gaertner. The Keuffel and Esser color analyser, sold by that company,[10] includes spectrometer, variable sector, and illuminating sphere, with holders for transmission (solutions) and reflection samples.

VI. Auxiliary Methods

It was noted in the introduction that several methods are available for supplementing and extending visual measurements; and it was there stated that the wide range of photometric sensibility of the eye gave it a general superiority to other methods in the visible spectrum. On the other hand, the eye has well known photometric limitations which often make visual work rather tedious. In most cases several readings at each wave length (5 to 10 or more, even in the brighter spectral regions) are necessary to secure the requisite precision.

Of the available auxiliary methods the photographic is no improvement in this respect; but the thermopile and photoelectric cell, when used with a galvanometer, furnish a means of measurement speedier and less tedious and requiring less skill in operation. So far as they are applicable, therefore, these methods are excellent aids or substitutes for the visual method.

All three methods—photographic, photoelectric, and radiometric—have been successfully and extensively used, especially in transmissive measurements. They are briefly described in the following sections, as regards spectral range applicable, essential apparatus and methods of operation, and factors affecting precision and accuracy.

[9] Schmidt & Haensch, Berlin.
[10] Keuffel and Esser Co., Hoboken, N. J.

1. PHOTOGRAPHIC

A. General Characteristics.—The photographic plate (or film), as a receptor of radiant energy, has some very desirable characteristics. One of these is the permanent record that is obtained, a property inherently possessed by no other detector. A second is that this record is an indication (within certain limits) of total energy received, rather than of the radiant power incident, as is the case with most other radiometers, including the eye. In other words, the photographic plate integrates the incident radiant energy, and by long exposures in the case of low radiant powers a record may be obtained possible in no other way. Moreover, the high sensitivity to the ultra-violet made it readily adaptable in a region where for a long time no other method could be used.

The above features have made photography the almost universal means for spectroscopic investigations. This is true not only in the blue, violet, and ultra-violet, where the ordinary plate is so highly sensitive, but also on both sides of this range by the use of specially prepared plates—throughout the visible and in the near infra-red on the one side, and in the extreme ultra-violet (Schumann and Lyman regions) and with x-rays on the other.

In spectroradiometry, however, the photographic method has been little used except for the spectral region covered by the ordinary plate, viz, the blue, violet, and ultra-violet. Various difficulties connected with the photographic plate when used as a radiometer (noted below) have precluded its use in regions where other methods are so readily applicable. Photographic methods have been used very extensively in spectral transmissive measurements, but only slightly in reflective measurements.

B. Essential Apparatus.—The essential apparatus for the measurement of spectral transmissive constants by the photographic method consists of: (a) a spectrograph, carrying the photographic plate, (b) a suitable source of radiant energy, (c) a means of varying the intensity of the radiant energy in a known way so as to bring two parts of the plate to the same density.

(a) Spectrographs of glass or quartz are available. The latter is the kind usually used, and is necessary if the ultra-violet region below about 320 mμ is to be studied. The usual glass prism absorbs all shorter wave lengths. The quartz spectrograph will transmit to the neighbor-

hood of 200 mμ.[11] The gelatine of the ordinary plate absorbs strongly in this region. Special plates are now on the market[12] which considerably increase the working sensitivity for these short wave lengths. Ordinary plates may be made sensitive to this region by treating with certain oils (**104**).

(b) For calibration purposes in the ultra-violet, no source is superior to the quartz-mercury arc. If this is not available, the various metallic arcs or sparks in air will be found suitable, provided care is taken to avoid those with too many lines. The danger to the eyes and skin, especially the former, from strong sources of ultra-violet radiant energy has already been noted.

Quantitative transmissive measurements by the photographic method are greatly facilitated by the use of a source of energy giving a continuous spectrum. For work in the visible and with a glass spectrograph, the usual incandescent electric lamps or gas flames are entirely suitable. The spectrum of such sources in serviceable amounts extends a short distance into the ultra-violet.

Various sources have been found to give a continuous spectrum throughout the usual ultra-violet range. The quartz-mercury arc, if run at red heat, will show a strong continuous spectrum upon which the lines are scarcely visible. The hydrogen discharge tube, under the proper experimental conditions and with quartz window, gives a continuous spectrum. A source which has proved very serviceable where constancy of intensity is not necessary is the high tension spark discharge under water. With pure distilled water and a Tesla coil discharge an intense spark one or two centimeters long may be obtained. The appearance of the spectrum is independent of the electrodes used, under the proper conditions. An approximation to a continuous spectrum is afforded by arcs or sparks in air with a large number of lines—such, for example, as the Jones electrodes. Under proper experimental conditions, a fairly strong continuous background appears with the various spark spectra.

(c) The methods of measurement of transmission by the photographic method, given a suitable source and spectrograph, are noted below.

C. Transmissive Measurements.—The density of an exposed and developed plate depends upon the following factors: (a) the wave

[11] Clear white fluorite will transmit much farther into the ultra-violet than quartz, but is extremely rare.

[12] Adam Hilger, Ltd., 75a Camden Road, London.

length of the radiant energy, (b) its intensity, (c) the time of exposure, (d) the time of developing, (e) the properties of the developer, (f) the character of the plate, (g) temperature conditions, and possibly other factors.

These many variables have practically eliminated the use of the photographic plate for transmissive measurements except by null methods. If two spectra from the same source are photographed on the same plate, thus undergoing also the same development, and at any given wave length the experimental conditions are such as to result in equal densities in the two spectra, all the above variables except intensity and time of exposure will be eliminated,[13] and at those wave lengths the intensities will be functions of the times of exposure. If the two exposure times are equal, the two intensities will be equal. If one intensity has been reduced by absorption within the material being examined and the other by some optical or mechanical means, a quantitative method is available for measuring the absorption or transmission, as in ordinary spectrophotometry.

The various methods used for such quantitative measurements up to 1914 have been summarized by Ewest (**97**). An abstract of this article in English has been made by Renwick (**97**). None of these early attempts at exact quantitative measurements of spectral transmission has proved as suitable as those described below, and the purpose of this report will be served by merely giving this one reference. Furthermore, it may be noted that Ewest's article properly does not include the *qualitative* method devised by Hartley and used so extensively by him and others since then, and described and illustrated, for example, by Kayser (**67**). This method, in brief, consists in photographing the spectrum of a given source successively through different thicknesses (or concentrations) and noting on the plate the "edges" of the absorption bands. The logarithm of thickness (or concentration) is then plotted against the wave lengths of these "absorption limits." This will result in a curve characteristic of any given substance. Without meaning to discredit the extensive investigations conducted by this method or to deny the value of the information thus obtained, it is emphasized that the method is strictly qualitative and that still more information would doubtless have been obtained if quantitative methods could have been used.

[13] This will be more certainly insured if the two points considered are on closely adjacent parts of the same plate.

The Hilger[14] "sector photometer" method (**98**) of measuring the transmissive constants of materials photographically, appearing in 1914, has proved with certain modifications a reliable and suitable quantitative method for both research and routine work. Lewis's similar method (**99**), while not so widely used as yet, should prove as serviceable as the other. This apparatus is also sold by Hilger.

In both instruments light from a single source is separated optically into two beams. One beam passes through the absorbing material being tested, and through a sector of constant aperture, as large as feasible, the other passes through a sector whose aperture may be successively decreased by known amounts. The two beams are then brought by suitable optical means on to adjacent parts of the collimator slit of the spectrograph. With proper adjustment there results on the photographic plate, for a given exposure, a pair of contiguous spectra, one of which has undergone absorption in certain regions, the other of which has been reduced in intensity throughout its whole length. At certain wave lengths the densities in the two spectra may be equal and at these wave lengths the transmissive constants of the material under test may be known from the relative apertures of the variable and fixed sectors. A series of exposures is, therefore, made for different settings of the variable sector, from which the complete transmissive curve may be obtained.

Hilger's and Lewis's methods differ in that the former uses rotating sectors with intermittent exposure, the latter an arrangement permitting of continuous exposure. In the latter also the radiant energy passing through the sample is in a parallel beam, a very desirable feature.

Lewis's design was purposely made to avoid the intermittent exposures of the Hilger instrument, as it had been supposed, on the basis of the Schwartzschild relation,[15] that the ratio of the sector openings on the latter instrument did not give the true transmissive values, but that a correction must be applied. The question has been discussed at length in Bureau of Standards Scientific Papers No. 440 (**103**), and it is there noted that the Schwartzschild relation cannot be strictly applied to the case of variable intermittent exposures but that the Abney

[14] Adam Hilger, Ltd., 75a Camden Road, London.

[15] $P/P' = (s'/s)^n$, where P and P' are two radiant powers incident for exposure times s and s', respectively, of such length that equal density results in the two cases. The exponent n is less than unity (for continuous exposures).

relation[16] also enters and in such a way that for the Hilger sector photometer true transmissive values may possibly be read directly from the sector openings. Experimentally, as summarized in the same paper, transmissive values so read have always been found to agree with values obtained by other methods within the errors of observation of th methods used. Various details connected with the Hilger apparatus, the spark discharge under water, the reading of the plates, etc., are given in the Bureau of Standards papers.

In addition to the sector photometer methods other quantitative methods have recently been tried (**100**; **101**; **102**), valuable perhaps for particular circumstances. Of special interest is the use of the wedge method by Plaskett (**105**) in solar and stellar spectroradiometry.

2. PHOTOELECTRIC

A. General Characteristics.—The electron emission of photoelectric cells under the action of radiant energy of the proper wave lengths furnishes another means of making transmissive or reflective measurements. Some of these cells are extremely sensitive and when used with an electrometer rival the eye in their ability to detect or measure small amounts of radiant power. The spectral range to which they respond depends upon the kind of metal used. Only the alkali metals show much response to radiant energy in the visible spectrum. Of these, sodium and potassium[17] are the only ones so far used for spectral transmissive or reflective measurements. Both sodium and potassium are sensitive to the ultra-violet but the response of potassium extends farther into the visible than that for sodium, the sensitivity curves for some of the cells extending as far as the red.

A question of first importance in the use of the photoelectric cell for quantitative spectroradiometry is whether or not there is a linear relation between photoelectric current and irradiation on the cell. It is sufficient to note here that cells constructed on the black-body principle—e.g., spherical surface with small window—obey approximately such a linear relation, and in fact some do exactly. However, it is never safe to assume without test that any cell does this. In certain methods of use as noted below, the question may be avoided.

[16] If a plate is exposed to a constant radiant power for time s (continuous) and then exposed for the same effective time s, made intermittent by means of a rotating sector, the density in the second case is less than that in the first.

[17] The most sensitive cells have the metal in the hydride form and contain some inert gas.

It may also be noted here that photoelectric cells must be operated in a dry enclosure. Ordinary humidity is usually fatal to proper working conditions. Moreover, the cells cannot be operated above a certain critical voltage without damage. It is, however, desirable to operate near this critical voltage, to obtain the maximum sensitivity of the cell.

Various details of general interest on the subject will be found in papers by Ives (**107**; **108**), Kunz (**110**), Coblentz (**111**) and in a recent report on photoelectricity by Hughes (**114**).

B. Methods of Operation.—The essential apparatus for photoelectric spectroradiometry consists of a suitable source of radiant energy, a spectrometer, a photoelectric cell with its applied voltage, a galvanometer, electrometer, or electroscope, and often auxiliary apparatus as noted below. These various items will depend upon the purpose to which the apparatus is put and upon the method employed. They can, perhaps, be best illustrated in connection with a brief description of some of the methods so devised.

Hulburt (**106**) with a sodium cell of his own design, measured the specular reflectances of a large number of metals in the ultra-violet from 380 to 180 mμ. He used the hydrogen discharge tube with quartz window as a source, obtained dispersion with a reflection grating, and measured the ratio of reflected to incident energy by noting the ballistic deflections of a quadrant electrometer.

The spectral reflectances of some of the alkali metals were measured photoelectrically in the visible by Nathanson (**109**), and in the ultra-violet by Frehafer (**113**). The former used an incandescent source, a glass prism spectrometer, and a quadrant electrometer (ballistically). He found it necessary to calibrate his deflections by means of crossed nicols. The latter used a quartz-mercury arc as a source, a quartz spectrometer, and measured relative photoelectric currents from the rate of motion of the gold leaf of an electroscope.

Gibson (**112**) has measured the spectral transmissive properties of glasses and dyes and the diffuse spectral reflective properties of papers in the violet, blue, and green, covering primarily the blue region where both the photographic and visual methods are relatively insensitive. He used two Kunz potassium cells and electrometer in a null method which eliminated the necessity of any study of the electrometer characteristics or the relation between photoelectric current and intensity. A glass spectrometer was used and an incandescent source. Recently a simpler method (**115**) for the transmissive measurements has been devised. A single cell and galvanometer are used, and by a combination

of the equal deflections method and a Brodhun variable sector a rapid direct-reading method has been effected. These methods have proved suitable for permanent apparatus for routine measurements.

3. RADIOMETRIC

The linear thermopile with galvanometer has proved a very efficient method of measuring spectral transmission for those wave lengths where sufficient radiant power is available. This applies throughout the entire infra-red, in which region a radiometric method is the only one possible. With the Mazda-*C* incandescent lamps as sources, measurements can be made throughout the visible, and with the quartz-mercury lamp at certain wave lengths in the ultra-violet. The most sensitive d'Arsonval galvanometers are sufficient for much work, but a large increase in sensitivity is possible with the Thomson galvanometer.

Dispersion may be effected by spectrometers of glass, quartz, fluorite, or rock salt, depending upon how far into the infra-red the measurements are to be made. A glass spectrometer can be used out to about 2.0 μ and is thus suitable for transmissive measurements for many solutions—e.g., water solutions of 1 cm or more thickness will not transmit beyond 1.4 μ. Beyond this range a spectrometer with prism of another material becomes necessary. A rock salt prism can be used out to 15 μ or beyond. The glass-inclosed incandescent lamp cannot be used much beyond 3 μ. For longer wave lengths the Nernst glower or gas mantles have been largely used.

For those interested in the use of the thermopile for transmissive measurements, various papers by Coblentz (**116**; **117**) will be instructive. The thermopile may be used, like the photoelectric cell, in a direct-reading equal-deflections method, instead of in the usual ratio-of-deflections method.

The bolometer and Nicols radiometer have also been used in transmissive measurements, but a further discussion of radiometric methods hardly falls within the scope of this report.

VII. MISCELLANEOUS

1. TRANSFORMATION OF SPECTROPHOTOMETRIC DATA INTO COLORIMETRIC SYSTEMS

It has been previously noted that spectrophotometric (or spectroradiometric) measurements form the only exact means of analysis of the stimulus of color and also form the most important specification of the color, such specification being fundamental and unique, independent

of material standards and independent of the observer. It suffers, however—as a means of *specification* not as a means of *analysis*—in that it cannot readily be interpreted as *color*.

By methods outlined in detail in the O. S. A. Colorimetry Report for 1921 (**4**) and by Ives (**119**; **123**), spectrophotometric data may be transformed into colorimetric systems. Because of the close correlation of the three color attributes, hue, saturation, and brilliance, with the three measurable light quantities, dominant wave length, purity, and relative brightness (*Cf.* Sec. II-5) and the fact that a specification in terms of these three physical quantities furnishes a complete and comprehensible *description* of the color in the fewest possible variables, such specification seems by far the most logical and suitable. As already noted, this system is usually called monochromatic analysis, although the term homo-hetero analysis is more exact.

The transformation of spectrophotometric data into the monochromatic system is accomplished by means of the three primary excitations. The method is completely described in the papers just referred to and will, therefore, not be repeated here. Special slide rules are available[18] to assist in these computations and in those of the next section. An extensive comparison between computed and experimental values by Priest and his associates (J.O.S.A. and R.S.I., *8*, pp. 28-29; 1924, and forthcoming papers) has shown the O.S.A. excitation data to be more generally reliable than those used by Ives, and also that for highly saturated colors they should be extrapolated beyond the values given. In Table 5 are given the excitation data taken from the Colorimetry Report, with the extrapolated values which have been thus found to give more exact results. Quoting from that report: "These values are for an equal energy spectrum. The relative magnitudes of the three elementary excitations have been chosen so that the curves for average noon sunlight have equal areas; that is, if the percentage values are plotted on a trilinear diagram sunlight falls in the center. The absolute excitation values are based upon a convenient arbitrary unit."

While it is admitted that the excitation data have a much too meager experimental basis, nevertheless the computed and experimental values of dominant wave length and purity check very closely; and pending further more exact determination of these three excitation curves they should be accepted as herein given.

[18] Keuffel and Esser Co., Hoboken, N. J.

TABLE 5.

Elementary Color Excitations

Used in computation of dominant wave length and purity from spectrophotometric data. Values (except as extrapolated) taken from Colorimetry Report, *J.O.S.A.* and *R.S.I.*, *6*, p. 549; 1922; which see for methods of computation.

Wave Length in millimicrons	Excitations		
	Red	Green	Violet
380			* 50
390			*130
400			253
410			433
420		* 1	614
430		* 3	915
440		7	1019
450		16	950
460	* 1	38	842
470	* 4	81	697
480	14	122	473
490	41	169	220
500	83	260	123
510	151	391	87
520	233	510	61
530	307	572	43
540	373	603	29
550	424	612	18
560	466	578	11
570	505	517	7
580	520	415	4
590	535	296	* 2
600	510	196	* 1
610	462	113	
620	375	59	
630	285	29	
640	195	10	
650	118	3	
660	68	* 1	
670	40		
680	22		
690	*13		
700	* 7.5		
710	* 4.0		
720	* 2.5		

* Extrapolated

2. COMPUTATION OF INTEGRAL LIGHT TRANSMISSION OR REFLECTION

Dominant wave length and purity values completely specify the chroma of a color, but the actual brightness must also be known before the color is completely specified. Probably in most cases, however, a more important quantity than actual brightness is the relative brightness as given by the integral transmission or reflection of the material for light. Along with dominant wave length and purity this may be done by means of the three excitations, but because of the uncertainty of their relative luminosities the values so computed will be less accurate than those computed from the integral luminosity, which may be accurately known.

The computation of relative brightness is somewhat simpler than that of dominant wave length and purity. Having given the relative spectral luminosity of the source by which the specimen is viewed, the computation of the integral amount of light from this source transmitted or reflected by the specimen is as follows: (a) Multiply the values of relative spectral luminosity of the source by the values of spectral transmission or reflection, wave length by wave length, the result being the relative spectral luminosity of the sample as viewed by the source; (b) compute, graphically or arithmetically, the relative areas of the two luminosity curves; (c) divide the area of the luminosity curve of the sample by that of the source, the result being the integral light transmission or reflection of the sample for that source.

The relative spectral luminosity of any source may be obtained by multiplying the relative spectral energy distribution of that source by the visibility of radiant energy. Visibility values will vary somewhat from one individual to another, but as a result of several extensive investigations the average visibility curve is more accurately known than is any other psychophysical function. Average values known as the I.E.S. mean values were adopted by the Illuminating Engineering Society (**6**) in 1918 and included in the O.S.A. Visual Sensitometry Report for 1920 (**2**). A revision of these I.E.S. mean values has recently been proposed (**35**) which results in better agreement with experimental data. The two sets of values are given in Table 6.

Relative spectral energy distributions vary, of course, widely from one source to another. Most of the common artificial sources follow closely a Planckian distribution, and spectral distributions of several such sources may be obtained from the Colorimetry Report. The

TABLE 6.

Standard Values of Relative Visibility

I.E.S. values: *Trans. I.E.S., 13*, p. 523; 1918; *J.O.S.A., 4*, p. 58; 1920.
Proposed values: *Bur. Stand. Sci. Pap.* No. 475, Table 3.

Wave Length in millimicrons	I. E. S. Adopted Mean Values	Proposed Standard Values*
400	0.0004	0.0004
410	.0012	.0012
420	.0040	.0040
430	.0116	.0116
440	.023	.023
450	.038	.038
460	.060	.060
470	.091	.091
480	.139	.139
490	.208	.208
500	.323	.323
510	.484	.503
520	.670	.710
530	.836	.862
540	.942	.954
550	.993	.995
560	.996	.995
570	.952	.952
580	.870	.870
590	.757	.757
600	.631	.631
610	.503	.503
620	.380	.381
630	.262	.265
640	.170	.175
650	.103	.107
660	.059	.061
670	.030	.032
680	.016	.017
690	.0081	.0082
700	.0041	.0041
710	.0021	.0021
720	.0010	.00105
730	.00052	.00052
740	.00025	.00025
750	.00012	.00012
760	.00006	.00006

* These proposed values were provisionally adopted by the International Commission on Illumination, meeting at Geneva, July, 1924.

Bureau of Standards[19] is about to issue charts and tables from which the Planckian distribution of energy from 400 to 720 mμ may be read for any color temperature between 1000° and 28,000°K.

Pending the establishment of standard white the spectral distribution for average noon sunlight at Washington may be taken as a standard on which to base not only the computations of integral light transmission or reflection, but also the values of dominant wave length and purity. These values are given in Table 7, along with those of a Planckian radiator at 5000°K.

3. GRAPHICAL PRESENTATION OF SPECTROPHOTOMETRIC DATA

An invaluable aid in the study of spectrophotometric data is their proper graphical presentation. One needs but compare a table with the graph of the same data to realize this. It is, therefore, a matter of importance that such graphs should be carefully prepared, so that the data may be readily grasped and not subject to misinterpretation. This matter has been discussed in a recent paper by Benford (**87**) who brings up several points of interest in this connection. As with all other parts of this report, the subject can be but briefly noted here. The following points may be mentioned:

Because of the widely varying problems in this field too much uniformity can not be expected. It is more important that the maker of such graphs be very explicit in his use of terms and strive to choose his coordinates in such a way as to bring out the points of interest and importance. For example, in plotting transmissive data, any one of the several terms of Tables 2 or 3 may be used, depending upon circumstances, but the use of the word transmission on the plot when transmittance or transmittancy is meant is very misleading.

On the wave length or frequency axis—the choice again being dependent on the circumstances of the problem—it is very helpful to insert the names of the hues as in Figs. 4 and 5, but dividing lines between the hues are misleading and should not be used.

The limits of the visible spectrum are even more indefinite than the dividing regions between the hues. It is perhaps a matter of choice whether 400-700 or 400-750 mμ (or other values) should be taken as the visible range. For most of the artificial light sources the region 700-750 mμ has as much luminous value as has 450-400 mμ, and on the

[19] Frehafer and Snow, Tables and Graphs for Facilitating the Computation of Spectral Energy Distribution by Planck's Formula. *Bur. Stand. Misc. Pub.* No. 56.

TABLE 7.

Values* of Relative Radiant Energy for White Light.

Abbot's values for average noon sun at Washington were tentatively adopted as standard white by the O.S.A. Colorimetry Committee, *J.O.S.A. and R.S.I.*, *6*, p. 560; 1922. The Planckian distribution at 5000°K has also been taken as standard white.

Wave Length in millimicrons	Average Noon Sun at Washington	Planckian Radiator at 5000°K ($C_2 = 14{,}350$ micron-degrees)
400	53.33	68.91
410	60.00	72.54
420	66.67	76.00
430	69.52	79.23
440	77.14	82.17
450	86.19	84.90
460	92.38	87.42
470	96.19	89.71
480	99.05	91.72
490	100.48	93.49
500	100.95	95.02
510	101.43	96.41
520	100.95	97.50
530	100.95	98.41
540	100.95	99.07
550	100.95	99.65
560	100.00	100.0
570	99.05	100.2
580	97.14	100.3
590	95.24	100.2
600	94.29	100.1
610	93.33	99.57
620	92.38	99.13
630	91.43	98.50
640	90.48	97.92
650	89.52	97.16
660	87.62	96.24
670	86.19	95.35
680	84.29	94.39
690	82.86	93.44
700	80.48	92.33
710	78.095	91.24
720	75.24	90.07

* Arbitrarily equal to 100.0 at 560 mμ.

usual prism spectrophotometer the two regions are about equally workable. However, the region 700-750 is usually of little importance in color specification.

For analytical purposes the actual values of the transmissive or reflective constants or the relative radiant energy should, of course, be plotted. They may be visually evaluated graphically in two ways: (a) by multiplying by the visibility values in the case of radiant energy data, and by the luminosity values of the source by which the material is viewed in the case of transmissive or reflective data; (b) by evaluating the wave length scale with reference to visibility or luminosity as is done by Benford. Either method may be advantageous for certain purposes, but both fall considerably short of expressing the color of the light or material (*Cf.* Sec. II-5 and 6, and Sec. VII-1 and 2).

Relative energy distribution curves have been commonly plotted to unity at 590 mμ. With the artificial sources of higher efficiency now in use, however, it is being found more convenient to assume the arbitrary value of unity at some shorter wave length. The wave length center of gravity of the average visibility curve is very close to 560 mμ, and this wave length is now being commonly used as the reference point.[20]

4. STANDARD SPECTRAL TRANSMISSION AND REFLECTION DATA

The collection and presentation of such data would be a work of considerable magnitude. If properly done, it should include a careful study of the reliability of the data. The present committee has been unable to take up this work and leaves it for the consideration of future committees.

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Except for the part on spectrophotometry the Bibliography does not pretend to be complete. The references given are those necessary for the particular purposes of the paper. Those chosen are usually the more recent ones and often contain extensive bibliographies which will lead one into a thorough study of the particular subject.

The attempt has been made, however, though doubtless far from successful, to include all references to original contributions in spectrophotometric methods (except perhaps as applied to the study of fluorescence and phosphorescence). References to much of the earlier work, especially the German papers, have been taken from Kayser's

[20] *Cf.* also M. Luckiesh, The Equality-point in Spectral Energy- and Luminosity-Distribution Curves of Illuminants. Jour. Frank. Inst., *183*, p. 633; 1917.

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Doublet Separations in Optical Spectra.—Having developed sparks in which multiply ionized atoms are abundant and emit their characteristic spectra, and a spectroscope by which these spectra (chiefly in the far ultraviolet) can be observed, Millikan and Bowen have measured characteristic frequencies of a number of atoms hitherto little or not studied. These include the series NV, CIV, BIII, BeII, and LiI (the Roman numeral is one unit greater than the number of electrons totally removed from the atom) each of these atoms having two inner electrons and one valence electron. The nuclear charges of these five atoms are $7e$, $6e$, $5e$, $4e$ and $3e$ respectively. Millikan and Bowen identify the first line of the principal series, due to the valence-electron, in each of the five spectra. This is a doublet and the frequency-difference of its components is measured; represent it by Δ.

The two components are emitted when the valence electron falls from one or the other of two outer orbits, the $2p_1$ and $2p_2$ orbits, into its stable orbit, the $1s$ orbit. Let us assume that the $1s$ orbit is a one-quantum circle, the $2p_1$ orbit a two-quantum circle, the $2p_2$ orbit a two-quantum ellipse, according to the familiar Sommerfeld theory. Let Ze represent the nuclear charge; let se represent the portion of this charge which is effectively cancelled by the two inner electrons (s should be 2 if the inner electrons are close enough to the nucleus, compared to the valence-electron). Then by the theory

$$\Delta = .365\ (Z-s)^4$$

The important discovery is that if we put in the observed values of Δ for the five specified atoms and calculate the corresponding values of s, we get quite plausible values in all five cases, ranging from $s=2.02$ for $Z=3$ (LiI) to $s=1.84$ for $Z=7$ (NV). This supports the theory as described. There is much other evidence of the same kind. Consider for example the series of atoms $Z=11, 12, 13, 14, 15, 16$, each with ten inner electrons and one valence-electron. Numerous doublets have already been measured in the spectra of these, and tabulations are given for those which constitute the first four lines of the principal series, the first two of the sharp series and the first of the Bergmann series. On calculating s for these by the preceding formula (with different values of the numerical constant, such as these orbits of higher quantum-numbers demand) plausible values are again obtained; s should be 10 for orbits lying far outside the 10 inner electrons, and the calculated values do approach and attain this amount for the orbits which are otherwise believed to be the largest. Similar agreements occur when s is calculated for the atoms $Z=5, 6, 7, 8$ with two inner and three outer electrons of which one figures as valence-electron; s ranges from 2.45 to 2.25, the outer electrons thus contributing to the screening effect; and there are computations for atoms with triplet spectra. However, these agreements are not perfectly welcome, for they traverse the accepted idea that the difference between the $2p_1$ and the $2p_2$ orbit is a difference in inner quantum-number (supposedly in the configuration of the inner part of the atom), and not in the shape of the orbit. If we reverse this idea, and reverse also the accepted idea that the difference between the $2s$ and either $2p$ orbit is a difference in shape of orbit and not a difference of inner quantum number, we lose several convenient explanations of fact, although perhaps no binding ones. The only alternative seems to be to add these agreements to the list of meaningless (?) coincidences in physics. It should be added that the values of s calculated from the *absolute* frequencies of the series-lines by the Moseley formula do not agree with these values except for remote orbits.—[R. A. Millikan and I. S. Bowen, Pasadena; Phys. Rev. *24*, pp. 209-228; 1924.]

KARL K. DARROW

PIPE LINE TEMPERATURE MEASUREMENTS

By Edward S. Bristol*

The present day cost of fuels available for the steam power plant is such as to make worth while sustained efforts on the part of the operating engineers to maintain high efficiency of heat utilization by giving attention to sources of possible loss that would have been considered of no practical consequence only a few years ago. As a result there is an increased demand for accurate instruments and measuring methods suited to the needs of the boiler room and the engine or turbine room. The precision and convenience of electrical methods prove to be of considerable practical advantage in this as in many other fields. Particularly adaptable to the steam plant are the types of electrical temperature measuring equipment known as the potentiometer thermocouple and the resistance thermometer systems. The temperature responsive element of either system can be inserted in a pipe so as to be in direct contact with the flowing steam; conditions favorable to accuracy and to minimum time lag in response to temperature changes are thus secured. The latter feature is of especial importance in pipe lines supplying steam turbines, where it is desired to detect immediately the presence of slugs of water in the steam in order to prevent erosion of the turbine blading.

For the purpose of acquiring a better understanding of the errors involved in applying an electrical temperature indicator or recorder to a commercial superheated steam pipe line the investigation here described was instituted. It was desired to learn the probable magnitude of the errors that would arise and also to determine upon the most suitable forms of temperature responsive element, from the standpoints of both accuracy and serviceability. For saturated steam the temperature of well covered pipe is only 1 or 2°F below that of the steam,[1] so that no appreciable errors should arise except those inherent in the measuring apparatus.

METHOD AND APPARATUS

Due to considerations of time and expense it was not feasible to conduct experiments with flowing steam. As a sufficiently close practi-

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[1] B. N. Broido, Trans. A. S. M. E., *44*, p. 1240; 1922.

cal approach to actual conditions it was decided to circulate hot air through a horizontal section of 8 inch extra heavy iron pipe, 3 feet in length, as shown in Fig. 1. This pipe was covered with a 1-1/4 inch layer of standard 85% magnesia lagging. The remainder of the system consisted of insulated stove piping to form a closed loop. Heat was supplied by eleven 500 watt so-called "space heaters," formed of high resistance wire wound on long flat strips. Current for the heaters was drawn from a 220 volt A.C. source and the air temperature was regulated by cutting the heating units in or out and by a rheostat in series with one unit. Air circulation was maintained by a small motor-driven blower which gave a center velocity in the 8 inch pipe of about 7 feet per second. The usual operating air temperature was about 600°F, a value representative of common steam practice.

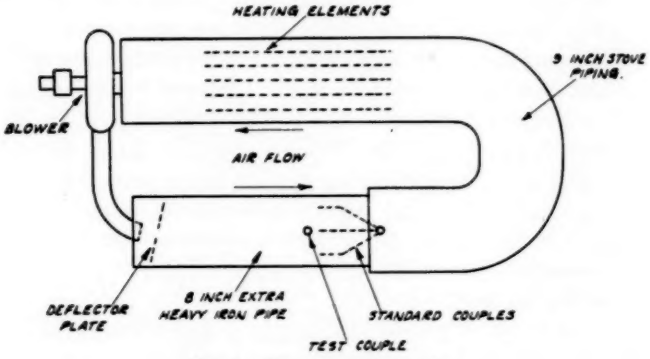

FIG. 1. *Plan view of apparatus.*

The standard temperature within the 8 inch pipe was determined with five No. 28 B. & S. gauge iron-constantan couples distributed with the hot junctions in a plane perpendicular to the pipe axis and about 9 inches from the downstream end of the iron pipe. These couples branched out as bare unsupported wires from the axis of the pipe at its downstream end, to which point they were led in from the exterior through small porcelain insulating tubes. The hot junctions were disposed one at the center and one every 90° around the circumference of a circle with a radius about 1-1/2 inches less than the inside of the pipe. Conduction error for the standard couples was practically eliminated by the 9 inch exposed lengths of wire adjacent the hot junctions and radiation error was made practically negligible by the small diameter wire. A tapped hole (3/4 inch pipe thread) for the insertion

of the test thermocouple or resistance thermometer was located in the top of the iron pipe about 1 inch upstream from the standard couple plane. Near the edge of this hole a No. 28 B. & S. gauge iron-constantan couple was embedded in the pipe wall to give the pipe temperature. The cold junctions of all couples in use were immersed in an oil bath for the temperature of which proper correction was made. All the couples used, both standard and test, were calibrated in an oil bath at about 575°F with the exception of the pipe wall couple, which was calibrated against the standard couples in the hot air system. A potentiometer was employed to determine the couple emf's.

As shown in Fig. 1, the apparatus is arranged in the manner finally found to be most satisfactory after a number of preliminary tests were run to learn how best to secure uniform temperature within the pipe. The direction of air circulation was at first the reverse of that shown and baffle plates were employed to mix up the air before it entered the measuring section. This arrangement was not as satisfactory, however, as discharging from the blower directly into the measuring section. With the final layout the extreme temperature variation at the standard couple cross-section was about 6°F and the temperature gradient along the pipe was about 8°F per foot.

It will be realized from the above description that the experimental conditions were such as to place the test couples and resistance thermometers at a disadvantage as compared with an installation in a steam pipe. Air has a specific heat less than half that for superheated steam and customary steam velocities range from 50 feet per second upwards, instead of the 7 feet per second employed in the tests. The possible rate of heat transfer to the test couples was therefore comparatively small. Because of the low heat carrying capacity of the air and the use of insulation thinner than that called for by the best power plant practice, the pipe temperature in the tests ran about 60°F below the heated air, as compared with a corresponding difference of 10 or 15°F for a well insulated pipe carrying superheated steam.[2] On this account the tendency to cool the hot junction by radiation and conduction along the couple wires was much increased. While these adverse conditions were unfavorable to couple accuracy, they were of advantage during the tests in magnifying the errors obtained with different types of couples and so indicating definitely when real improvements were made.

[2] From data obtained by Chrs. Eberle of Munich and quoted in Trans. A.S.M.E., *44*, p. 1201; 1922.

After completing the series of tests in the manner outlined, with the pipe about 60°F cooler than the circulating air, it was considered desirable to run further tests of the most promising types of thermocouple and resistance thermometer under conditions more nearly approaching those of actual superheated steam service. To accomplish this end it became necessary to raise the pipe temperature closer to that of the air. Increased thickness of pipe insulation proved to have little effect, but by adding water vapor to the system it was possible to reduce the temperature differential to about 30°F. The water vapor was also found to give a more uniform air temperature within the pipe,

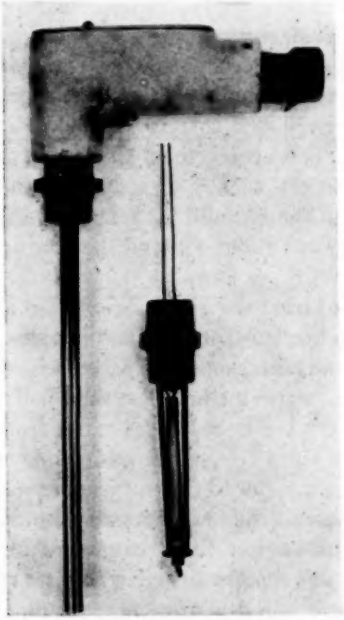

FIG. 2. *Pipe plug types of resistance thermometer and thermocouple.*

reducing the extreme variation at the cross-section covered by the standard couples from about 6°F to less than 3°F. One test was made with the pipe only 15°F below the air. However, this small difference was attained by heating the system too high and then cutting off the heating current entirely. The air cooled more rapidly than the pipe, so that a small temperature differential was thus secured. All the temperatures were drifting during this run, so that the results obtained are less dependable than those for the remainder of the tests. In every

other test the system was allowed to "soak" for about four hours after bringing the air up to temperature, in order to attain a condition of equilibrium, with the pipe as hot as it could be made for the given air temperature. A solitary test was run with dry air at about 370°F and the pipe some 30°F cooler.

The basic type of thermocouple used is shown in Fig. 2. Its construction is somewhat like that of a spark plug. The two wires are brought out through separate tapered insulating bushings held in conical

TABLE 1. *Results of Pipe Line Temperature Tests*

General Conditions
8 inch extra heavy pipe, lagged
Center velocity of circulating hot air = 7 ft/sec.
Test Conditions (approximate)

Condition symbol	*A*	*B*	*C*	*D*
Circulating air temperature (°F)	600	370	600 drifting	600
Pipe temperature (°F)	540	340	585 drifting	570
Air condition	Dry	Dry	Vapor added	Vapor added

Readings with Platinum Resistance Thermometers

Active Stem Dimensions	Conditions	*Errors °F	
		Based on Average Temp.	Based on Center Temp.
7/16" diam., 6¾" long, No. 20 gauge wall	Plug exposed exterior to pipe A	−14½	(−16½)
	Same, plug lagged A	−11½	(−13½)
7/16" diam., 7½" long, No. 20 gauge wall	Plug lagged D	− 6	(− 7½)

* The average temperature forms the true standard from which should be computed the error for a resistance thermometer extending across the pipe or a thermocouple with a shielding tube similarly disposed. For a directly exposed thermocouple with its hot junction on the pipe axis the error should be based on the indication of the center standard thermocouple. The errors computed on both bases are given in the table to more fully record the actual test conditions. Parenthesis marks enclose the figures which are not the true errors.

seats, so that there is nothing to blow out under high steam pressures. Fig. 2 also illustrates the platinum resistance thermometer employed, with its round nickel-silver protecting tube suited to steam pipe service. The test results obtained are summarized in the accompanying table.

DISCUSSION OF RESULTS

Very little time was spent in testing resistance thermometers, as no important modifications of structure were possible. The average tem-

perature for the pipe section is the standard from which the error should be computed in this case, although the figure based on the maximum or

TABLE 2. *Results of Pipe Line Temperature Tests, con.*

Thermocouple Details					*Errors °F	
Form (See Fig. 3)	Material	Wire Size	Active Length	Test Condition	Based on Aver. Temp.	Based on Center Temp.
(1)	Iron-Cons.	No. 16	4″	A	(−18)	−20½
(2)[1]	"	"	"	A	(−16½)	−19½
(2)	"	"	"	B	(− 7½)	− 9
(2)	"	"	"	C	(−10½)	−10½
(2) Porcelain entirely removed	"	"	"	A	(−18½)	−22
(3)	"	"	12″	A	(−18)	−20
(4)	"	"	"	A	(−16)	−19½
(2)	Copper-Cons.	No. 8	4″	A	(−44)	−47½
(2)	"	No. 16	4″	A	(−14½)	−18
(2)	"	No. 22	4″	A	(−23)	−26½
(2) Porcelain removed from lower 7/16″	"	"	"	A	(−15)	−18½
(2) Porcelain removed from lower 15/16″	"	"	"	A	(−11½)	−15
(2) Porcelain entirely removed	"	"	"	A	(− 9½)	−13
(5)	"	"	5½″	A	(+ 1)	− 3
(5)	"	"	"	D	(− ½)	− 1
(2)	"	No. 28	4″	A	(−13½)	−16½
(2) Porcelain removed from lower 1¾″		"	"	A	(+ 6)	+ 1½
(5)	"	"	5½″	A	(+ 4)	+ ½
(2) Couple encased in polished tube[2]	"	No. 16	4″	D	− 7½	(− 9)
(2) Couple encased in blackened tube[2]	"	"	"	D	−16	(−17½)
(5) Bare length encased in polished tube[3]	"	"	5½″	D	(− 7)	− 9
(5) Bare length encased in blackened tube[3]	"	"	"	D	(−12½)	−14½

[1] The plugs of all the following thermocouples were lagged (exterior to the pipe).

[2] Nickel-silver shielding tube extending across pipe. 7/16″ diameter, 7½″ long, No. 20 gauge wall.

[3] Nickel-silver shielding tube extending along pipe axis. 7/16″ diameter, 2″ long, No. 20 gauge wall.

* See note at bottom of Table 1.

center temperature is also given in the table. It appears worth while to lag the exposed head of the type of resistance thermometer used, since

the error was reduced thereby 3°F at a temperature of 600°F. It is rather surprising to note that the resistance thermometer with a 7/16 inch diameter stem proved superior to a No. 16 gauge thermocouple (a common commercial size). This superiority is dependent upon the existence of a fairly bright stem surface. Should the thermometer stem become darkened the radiation error would increase and the advantage disappear.

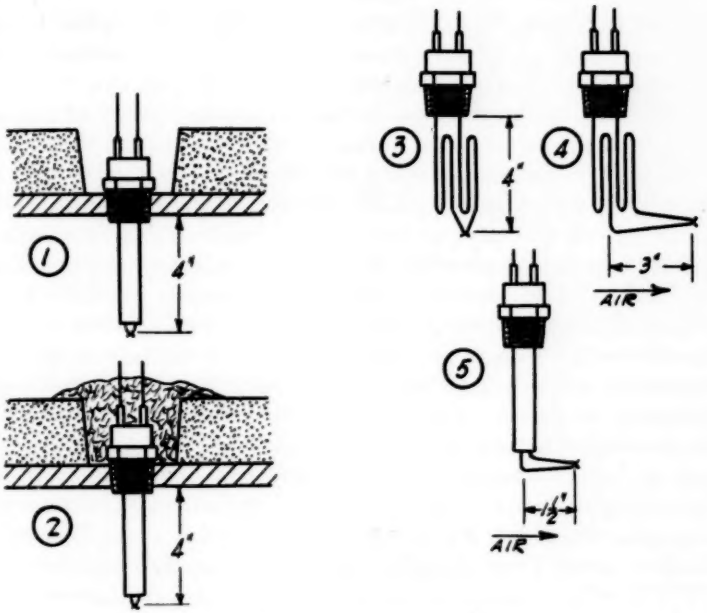

FIG. 3. *Forms of thermocouples tested.*

As the hot junction of every couple tested was located at the center of the pipe, the error should be computed from the center temperature; except for the two cases in which a shielding tube extending across the pipe was used, when the average temperature should form the standard. The maximum probable error of method in the thermocouple results is of the order of 2°F.

Inspection of the thermocouple results shows first that lagging of the exposed portion of the plug type employed reduced the error by only about 1°F and is therefore of little use except for the smaller and more accurate forms of couples.

The No. 16 gauge couples proved to be remarkably independent of any modifications of form or material. Increase of the length of path from the hot junction to the pipe failed to lessen the error. Also, changing one of the couple elements from iron to copper raised the indicated temperature, instead of lowering it as might have been expected from the greater heat conductivity of copper. These two results show that conduction is a negligible source of error for this size of couple under the test conditions.

Such a large error was obtained with the No. 8 gauge copper-constantan couple that no modified forms were tested. It is probable that conduction is an appreciable source of error for this size.

Comparison of the three smaller sizes of copper-constantan couples tested in unaltered form No. 2 does not show a consistent decrease of error with wire diameter, as might be anticipated. The hot junction of this type of couple derives its heat from the air flowing past and is presumably cooled more or less by the porcelain insulator, which radiates heat to the pipe walls. With small wire sizes it is conceivable that the resultant effect of these two actions may be appreciably influenced by the nature of the contact between the wires and the porcelain tube. Thus, if the wires did not touch the tube at all for a considerable distance back from the hot junction, the latter would get hotter than for the case of contact nearer by. When the porcelain tube was partially or entirely broken off the couple error decreased progressively and at a diminishing rate with the wire size, as would be expected.

It will be noted that the No. 22 gauge couple in form No. 5 indicated a temperature within 1°F of the center standard couple. As this degree of accuracy was obtained with a hot air to pipe differential of 30°F it is believed that such a couple will meet any practical accuracy requirement in a lagged steam pipe. While the No. 28 gauge couple in a similar form is of course slightly more accurate, it is too delicate to meet service conditions.

In view of the superior performance of the resistance thermometer as compared with the common commercial size of thermocouple, No. 16 gauge, some tests were made with shielding tubes for the latter. With such a tube polished it will be noted that the thermometer accuracy was very nearly equalled. Blackening the tube greatly increased the error but a resistance thermometer would of course be affected in the same way. It is interesting to observe that there was no appreciable difference for a couple shielded with a polished tube whether the tube extended across the pipe with no air circulation through it or whether

it was placed parallel to the pipe axis so as to permit of maximum air flow.

The important conclusions applying to lagged superheated steam pipe conditions that can be drawn from this series of tests are as follows:

1. The error of a plug type No. 16 B. & S. gauge copper-constantan or iron-constantan couple (form No. 2) may reach $-10°F$ under the worst conditions apt to be found.

2. A No. 16 gauge couple enclosed in a bright nickel-silver tube will have its accuracy slightly improved thereby as long as the tube surface remains undarkened.

3. For maximum accuracy requirements a No. 22 gauge couple in form No. 5 can be used with the assurance that the error will not exceed $-2°F$.

4. A resistance thermometer of the type tested and with an undarkened surface will have a maximum error of about $-5°F$ under the worst service conditions.

The two chief factors affecting the performance of a temperature measuring device inserted in a superheated steam line are: First, the temperature difference between the steam and the pipe, and, second, the degree of stratification of the steam. Only the effects of the first have been considered in the investigation here reported. In actually measuring superheated steam temperature, however, it is essential where accuracy is desired to choose a point in the pipe line where the steam is well mixed. It appears desirable to call attention to this fact before closing, as the choice of an unsuitable location (such as near a superheater outlet) for the measuring element may easily give rise to errors far in excess of any that will result from an incorrect type of instrument.

LEEDS AND NORTHRUP CO.,
PHILADELPHIA, PA.

Positive Currents into Sounding Electrodes Immersed in the Positive Column of the Mercury Vapor arc.—This is a partial report on work done at the Siemens laboratory, evidently running parallel with Langmuir's investigations upon the current received by a negatively charged electrode dipped into a mercury vapor arc. After a previous divergence of opinion the authors concede Langmuir's interpretation, which is, that the electrode is surrounded by a sheath from which electrons are excluded by virtue of its negative potential, and across which positive ions flow forming a current of a single sign; the current density (which is constant after the potential falls below a few volts negative) being determined by the density of ions in the

mercury vapor, the voltage across the sheath by the applied potential, and the width of the sheath by these two quantities according to the familiar space charge equation. The sheath is visible as a dark stratum lying along the electrode, which in Schottky's experiments is a cylinder with a heating coil wrapped around it and a thermocouple attached to it. Various values of potential E are given to the cylinder, the corresponding readings of the thermocouple are recorded, and subsequently a current is sent through the heating coil and adjusted till the same readings are reproduced; thus the rate at which heat is generated by the impact of positive ions on the cylinder is determined as a function of the ion-accelerating voltage. The values obtained are all compatible with the ones calculated, from the assumption that the ions fall across the sheath and strike the cylinder with the full energy acquired from the P.D.; this confirms the general interpretation (as opposed to the earlier one that the current is an electron efflux from the wire, for electrons would shoot so far into the gas that their energy could not return as heat to the electrode). Schottky also observes indications of heat set free when electrons strike the cylinder (the voltage being reversed in sign), that is, the thermionic cooling effect reversed; for surface-potential-drop he deduces 4 to 5 volts for Fe and Ni; but he prefers to subdivide his publications and reveal these data elsewhere.—[W. Schottky, J. V. Issendorff; ZS. f. Phys. *26* pp., 85-94; 1924.]

KARL K. DARROW

Arcs Maintained with Cold Cathodes.—While it has always been believed that an arc cannot be maintained if its cathode is prevented from becoming and remaining incandescent (partly because of experiments by Stark and Cassuto who found it impossible to maintain an arc between a stationary anode and the edge of a swiftly-revolving wheel as cathode) Stolt makes the surprising announcement that an arc can be kept going while its cathode-end travels around so rapidly over a metal plate that the plate nowhere becomes too hot to touch with comfort. The experiment is performed either by revolving the metal plate under the arc, or by revolving the arc over the metal plate by applying a radial magnetic field. The chief condition for success is that a very well-polished plate be used; the experiment succeeded with Cu, Au, Ag by the first method, with Cu and brass by the second. Speeds of 6 m/sec of the relative motion of arc and plate, arcs as long as 4 mm, were attained. The arc does not show a bright continuous spectrum at the cathode end as incandescent metal if present should furnish. This result if verified is liable to vitiate the theories of the arc, which are generally based on the presumed fact that the cathode is of necessity incandescent and therefore able to send out abundant electrons, or else yields a greater number of secondary electrons per impinging positive ion when hot than when cold.—[H. Stolt, Upsala; ZS. f. Phys. *26*, pp. 95-101; 1924.]

KARL K. DARROW

A QUICK-ACTING DYNAMOMETRIC CONTACT SPRING

By F. J. Schlink

The device herein described may be termed a force-increment recorder. The purpose of the investigation was to devise a means of making an electrical contact so as to record in an oscillograph sensibly without time lag, the instants of the inception and cessation of the lifting force on a vertically sliding rod carrying a number of brushes traversing a bank of contacts. The sliding rod was driven upward by friction of a flat elastic strip at its lower end pressed against a continuously revolving roll by the action of a magnetic relay. When the relay was de-energized, the strip moved away from the roll and the upward motion ceased, the brush-rod being held in the position attained at the time of action of the relay, by the operation of a ratchet and pawl. It was required to measure the short time interval elapsing between the instant of opening of the relay circuit and the cessation of the impulse driving the brush-rod upward, the lag being due to the time of operation of the relay and the time required for the flat driving strip to spring out of contact with the revolving roll. Since this lag was known to be very small, it was essential that the lag in the lag-measuring device itself should be very small.

The first solution of the problem, carried out in cooperation with Mr. E. H. Flath, involved the use of an overfilled microphone button, the usual Western Electric button being modified by substitution of sheet micarta rings for the mica insulating rings at each end (the mica being too weak flexurally to carry the loads involved) and by increasing the amount of granular carbon contained, a change necessitated by the use of the button with its axis at 90 degrees to its normal position. This arrangement, as might be expected, proved sensitive, but afforded little or no control of the force end-point at which contact should occur, which during the later development of the problem turned out to be a desirable improvement.

The following simple means was then assembled for opening the circuit to the oscillograph at the instant of cessation of up-drive force. The principal structure of this device consists of an ordinary machinist's micrometer caliper introduced into the vertical rod $N\,N'$, through which the switching mechanism is lifted. This rod is cut and supplied with suitable clamps for the purpose. Primarily the caliper is used as a stiff

spring having a very high natural frequency, so that when it is deflected by change in the load on rod N, it will move toward its new configuration in a period of time quite negligible in comparison with the lag which is to be determined, in the magnet and linkage.

To the moving tip of the micrometer screw and exactly on the axis of the screw is affixed by suitable cement (celluloid, or hard de Khotinsky) a well polished steel ball, Y, of the sort used in ball bearings; to the fixed anvil of the micrometer and likewise in line with the axis of the screw, is affixed an identical ball, Z, but this second one is electri-

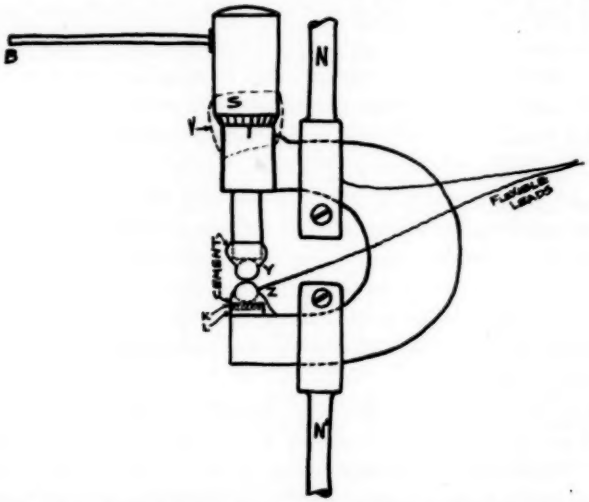

FIG. 1. *Null-type electrical contact dynamometer using screw micrometer as quick period spring.*

cally insulated from the micrometer frame by being cemented to a hard, solidly seated insulating disk or ring, K, which is first secured to the anvil L. A fine flexible wire is connected to the micrometer frame and another to ball Z, the latter most easily, probably, by butt-soldering at a low temperature, or by the conducting cement used in incandescent lamp manufacture.

A very small current is now led through the ball contacts, by an external controlling resistance and a dry cell, a milliameter in series being used as an indicator for convenience in adjustment. The micrometer spindle is turned very delicately until contact is just broken when the net load transmitted through the upper part of the rod N is zero.

A slight pressure added to the dead load on the rod will close the contact by reducing an air gap of the order of .1 μ. So small is this gap that the final adjustment of the ball contacts through the turning of the barrel S can only be done by repeated trial and error, that is if considerable definiteness in the value of load at closing of the contact is wanted. Thus it has been found convenient to attach to S a long light arm B which can be tapped very lightly to move the upper ball up or down through a small fraction of a micron. The setting of the contact gap is greatly stabilized by the application of a ring of viscous or plastic material, say soft wax, around the barrel of the micrometer at the region indicated at V. This damps down any small lost motion or shake in the screw and keeps the adjustment quite stable when once the critical position of the balls has been found. The whole arrangement is naturally quite sensitive to temperature changes; so true is this in fact that a change of local temperature of a degree or so may be used as a fine adjustment to establish the exact load end-point desired in the closing of the ball contact. It will be understood that the micrometer caliper applied to this purpose is merely a convenient and ready combination of a very stiff and anhysteretic spring with a rather delicate adjusting screw built in and adapted to setting the zero of registration of the spring as a dynamometer. It is evident moreover that the method could be elaborated by the use of two or more of the dynamometer contact springs in series, so as to permit of the determination of several points on the load-time or load-displacement curve. (A means by which displacements executed at very high speed may be recorded oscillographically will be described in a forthcoming paper). In such cases it would probably be desirable to construct a much lighter deflecting system by building the screw-adjusted U-springs specially for the purpose; so constructed they could be made very small and light and so possess an even quicker period than the micrometer frame described. Likewise the balls used in such a device could be much smaller, perhaps a millimeter or less in diameter.

If the registration of the instrument is to be recorded by the oscillograph, the ammeter used for setting up and adjusting should be provided with a shunting switch to minimize the inductance of the circuit when oscillograms are taken.

If the device is to be used over an extended period of time, it will be found that a drop of neutral oil applied between the balls will prevent atmospheric depreciation of the highly polished contact surfaces. The contact conditions are so delicate, on account of the extreme stiffness

of the micrometer frame, or other U-spring[1] used that the greatest care should be used in the selection of the balls, in lining them up axially, in protecting them from dust and moisture, and against an excessive current flow. The contact can handle perhaps 20 or 30 milliamperes without excessive depreciation, but the less required for the registering device, the better, for obvious reasons. The great stiffness of the micrometer frame and the hardness and elasticity of the balls makes the device substantially immune to mechanical shocks in use, at least up to gross loads of several kilograms (which do not reach the screw itself if the contact adjustment is at or near zero net load). Firmness of seating of the two balls, especially of the one resting on the insulating disc, is very important, as difficulties in obtaining a reproducible setting of the contact-making load under steady temperature conditions are to be ascribed mainly to irreversible movements or strains at this point. Even with the ordinary rough shop micrometer, stability of load at opening of the contact, after steady temperature conditions are reached, may be relied upon to 10 grams or so; probably much better if a lower current strength through the balls, and other evident refinements, be used.

The particular utility of two balls as contacts, as compared with a point and plane, or a ball and plane, lies in the fact that an invariably located point contact can be assured with a minimum of shop work. The balls as commercially produced, afford very smooth, hard, and resilient surfaces; whereas if a ball and plane contact were used, there might be some difficulty on this score and certainly renewal and readjustment of one of the surfaces would not be so easy or so rarely needed as with the means described.

AMERICAN ENGINEERING STANDARDS COMMITTEE,
NEW YORK CITY,
NOV. 1, 1924.

Spark Spectrum of Cs.—361 lines of this spectrum between 3268A and 7280A are photographed and measured to hundredths or thousandths of an Angstrom. It is excessively complicated, as to be expected from the electron arrangement in ionized Cs; an incipient analysis of it shows similarities with the spectra of Xe and Ne. The series in the arc spectrum are also traced as far out as the lines originating in the 5*s*, 7*d* and 8*f* orbits. The spectrum is obtained from an intermittent condensed discharge in a mixture of Cs vapor with He gas, and rules for best producing it are given.—[L. A. Sommer, Munich, Ann. d. Phys. *75*, pp. 163-181; 1924.] KARL K. DARROW

[1] A circular or ring shaped spring can also be used to advantage when the load sensibility required is not so high as the U-form affords.

A TILTOMETER MADE OF FINE TUNGSTEN WIRES

By Enoch Karrer and A. Poritsky

GENERAL DESCRIPTION

Incidental to our study[1] of losses from fine hot wires with a view to current control there have arisen several other applications of fine hot wires. Among these is an instrument for indicating position relative to the direction of gravity. We have chosen to name this instrument a "tiltometer." It consists essentially of four fine tungsten wires arranged to form a miniature Wheatstone bridge whose opposite branches are juxtaposed. The whole Wheatstone bridge is mounted in a lamp bulb with four leads passing through the stem of the bulb in precisely the manner in which it is done in ordinary lamp practice. The bulb is filled with the gas used in the Mazda C lamps and at the same pressure as in the lamps.

To two of the leads is attached a source of electric power, while to the other two is connected an instrument for measuring current (such as a galvanometer or milliammeter). When the bulb containing the bridge through which a current is flowing is rotated the galvanometer index will deflect.

DETAILED DESCRIPTION

The detailed construction and operation of the tiltometer will be clear by reference to the figures. A diagrammatic sketch of the electrical circuits is shown in Fig. 1. The fine tungsten wires constituting the four branches of the Wheatstone bridge are numbered 1, 2, 3, 4. We let the branches 1 and 4 be opposite each other in the ordinary Wheatstone bridge set-up. They are juxtaposed here because their effects are the same so far as the deflection of the galvanometer is concerned. Likewise, branches 2 and 3 are placed near each other. (The four corners of the Wheatstone bridge are AA, BB, CC, DD, Fig. 1). The battery E connected at points A and C furnishes current through the bridge. The milliammeter which indicates the balanced or unbalanced condition of the bridge is connected to points B and D. The rôle which the independent circuit H in series with battery F plays will be made clear presently.

[1] This work was completed several years ago in the Nela Wesearch Laboratories. It was well under way before the papers on this and related subjects by Davis, Paris and Tucker and several others came to our notice.

In this experimental form each of the four wires (1, 2, 3, 4,) has two independent leads L going through the stem S, so that all connections were made outside the bulb B. When the current through the bridge is sufficient to heat the wires appreciably this system may be quite sensitive to their relative positions, with respect to the convection streaming. That is, if the bulb containing the bridge is rotated around a horizontal axis parallel to the wires themselves, the bridge will become more or less unbalanced on account of the change in resistance of branches 1 and 4 or 2 and 3. The change in resistance due to a change in temperature is brought about by the transference of heat to or from the convection streams that pass the wires. When in the horizontal plane, the two pairs of wires may be equally affected by the convection streaming, but when one pair is (say) immediately below the other, it is cooled more than the other and the balance of the bridge is upset.

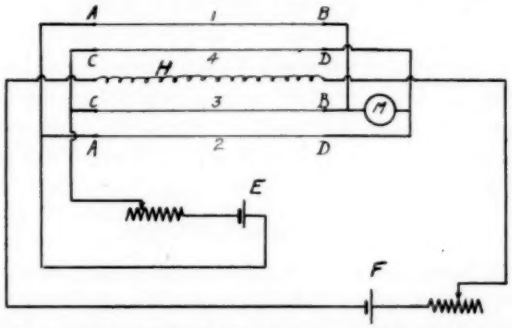

FIG. 1.—*Diagrammatical sketch of electric connections in Tiltometer. Tungsten wires 1, 2, 3, 4 constitute branches of Wheatstone Bridge. H—heater; E—bridge battery; M—milliammeter; F—heater battery.*

The sensitivity of the device depends upon the violence of the convection streaming. This in turn depends upon the magnitude of the losses due to convection and conduction in the gases. In order to maintain a more vigorous convection streaming we have employed an auxilliary heater H, Fig. 1, entirely independent of the bridge. This heater may take the form of a filament of suitable size or it may be a helix of wire. The latter form offers some advantages, and we have found that the tungsten wire helices used in the gas filled Mazda lamps are very satisfactory. This heater necessitates two additional leads when used thus independently. However, the heater may be connected in series with the bridge and four leads will still suffice.

In Fig. 2. are shown some constructional details and the relative size and position of parts of a tiltometer in which the wires are tungsten filaments such as are used in the standard 40 watt mazda B lamps; and the heater is a coil such as is used in the 50 watt mazda lamp. A curve showing the performance of a tiltometer constructed along

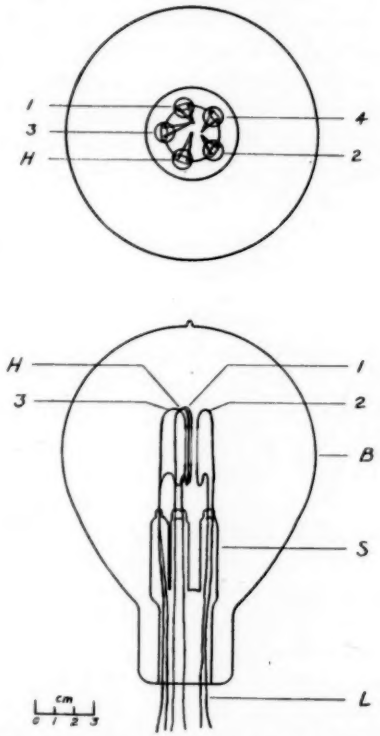

FIG. 2.—*Tiltometer—cross-section and elevation. Drawn to scale. In this experimental form each of the 4 wires as well as the heater has 2 independent leads.*

these lines is given in Fig. 3, when the current is 0.60 ampere through the bridge and 0.32 through the heating coil. The voltage across the latter was 6.9 while across the former with some resistance in series it was 2.2 volts. The ordinates of the curve are millivolts[2] when divided

[2] Measured with a millivoltmeter with range of 50 millivolts over a scale of 150 divisions. Resistance 0.935 ohms.

by 3. Under slightly different conditions the curve in Fig. 4 represents the performance of this tiltometer. Here the bridge current was only

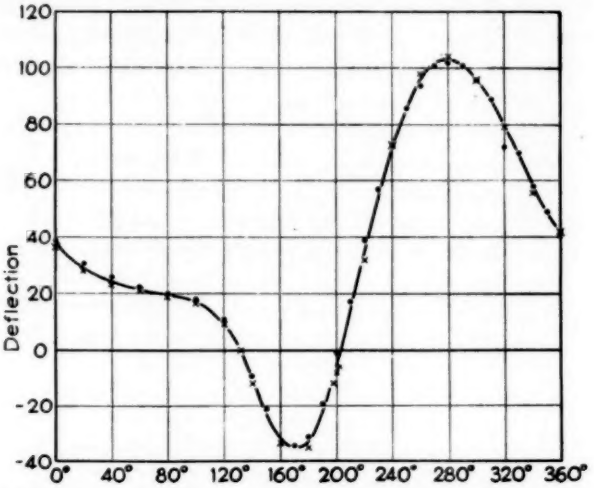

FIG. 3. *Relation between deflection and rotation of a tungsten wire tiltometer with coiled heater 2.2 V, 0.60 A in bridge; 6.9 V, 0.32 A in heater.*

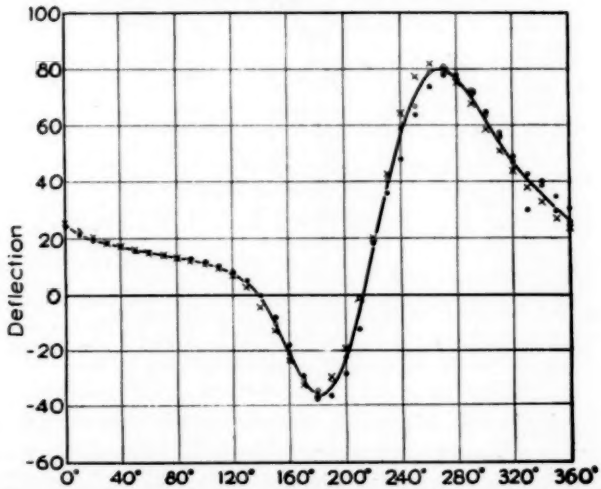

FIG. 4. *The same relationship for the same tiltometer as in Fig. 3. 0.9 V, 0.1 A in bridge; heater same as in Fig. 3.*

0.1 ampere with a voltage of 0.9 (i.e. including again some resistance in series); while the heater voltage remained unchanged. In this

tiltometer a rotation of 110° gives the whole deflection (i.e. the sum of the two maxima) which is about 140 on the millivoltmeter scale. The amount of rotation required to give the whole deflection in any given tiltometer depends upon the relative angular position of the two pairs of wires. In the present case it was intended that this should take place within 90 to 100°.

The photograph of Fig. 9 shows this tiltometer mounted for demonstration. For this purpose the heating coil is connected in series with the bridge, and in series with a 10 volt battery and a small resistance such that 0.2 ampere flows through the tiltometer. The indicating instrument is a microammeter of 83 ohms resistance, whose full scale represents about 106 microamperes. A rotation of 45° causes a deflection of 100 microamperes under these conditions. A rotation of about 110 gives the whole deflection which is some 180 microamperes.

PRELIMINARY EXPERIMENTS—DATA ON OTHER TYPES OF TILTOMETERS

During the preliminary experiments we made tiltometers with fine iron wires instead of tungsten filaments. These are of interest in several respects. We have more detailed data in some of these cases than we have for the final form of tiltometer using tungsten filaments. The fact that the sensibility is occasionally greater than in the tungsten tiltometer is not to be given any weight. We have in neither case arrived at the most sensitive construction. The use of tungsten wire has an inestimable advantage in that the technique of a great industry is immediately at our command.

In Fig. 5 are curves pertaining to a tiltometer made of iron wires about 1.5 cm long and 0.05 mm diameter. The auxillary heater was a tungsten coiled filament. In this case the rotation that produces the whole deflection is about 90°. Of course, a rotation equal to the supplement of this angle, i.e. 270° will also cause the same deflection. In the former case we have high sensitivity—for the latter a much lower sensitivity. However, this kind of response (i.e. such as we have for the larger rotation giving the whole deflection) may be of interest under certain conditions. It allows rotation with little response for a certain range, and gives great response for any rotation beyond this range.

The different values of voltage to which the curves relate include a potential drop across the resistance[3] which was always in series with the Wheatstone bridge. The actual voltage across the bridge is considerably

[3] Unfortunately no record was made of this resistance.

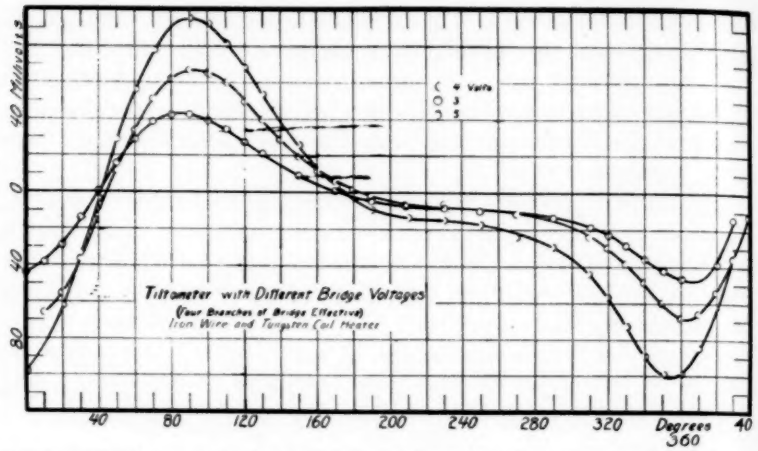

FIG. 5. *Deflection vs. rotation for a tiltometer with iron wire in bridge and tungsten coil heater.*

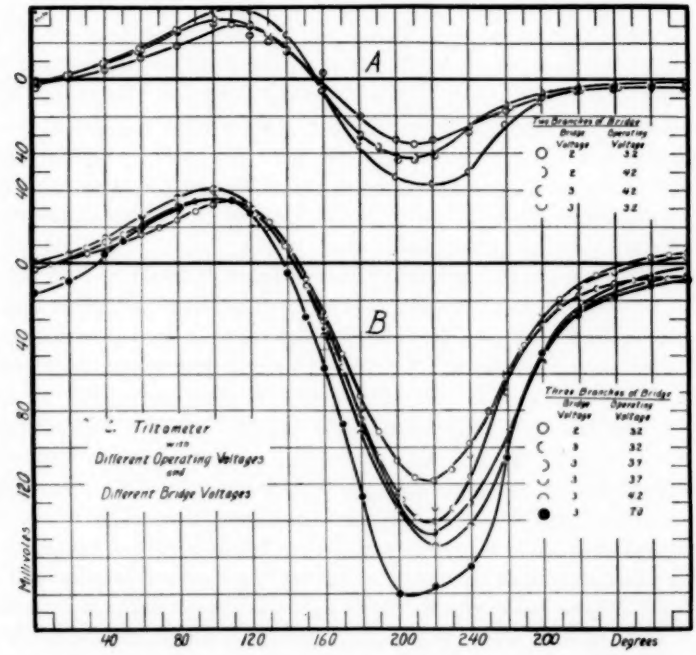

FIG. 6. *Deflection (millivolts) vs. rotation for a tiltometer with iron wire (.05 mm) in bridge and tungsten coil heater, for different bridge voltages and heater (operating) voltages.*

less. To maintain a current of .16 ampere for example, through the bridge itself only about 0.17 volt is required.

In Fig. 6 are given curves relating to a tiltometer with iron wires and tungsten coil heater. The iron wires are of the same dimensions as in the previous tiltometer. The tungsten wire heater was made of a portion (2.8 cm) of the coiled filament used in the 250 watt Mazda lamp. The upper set, *A* Fig. 6, of curves refer to the bridge when only two branches (i.e. two wires) are effective. In the remaining two branches two resistances were connected instead of the wires. Several

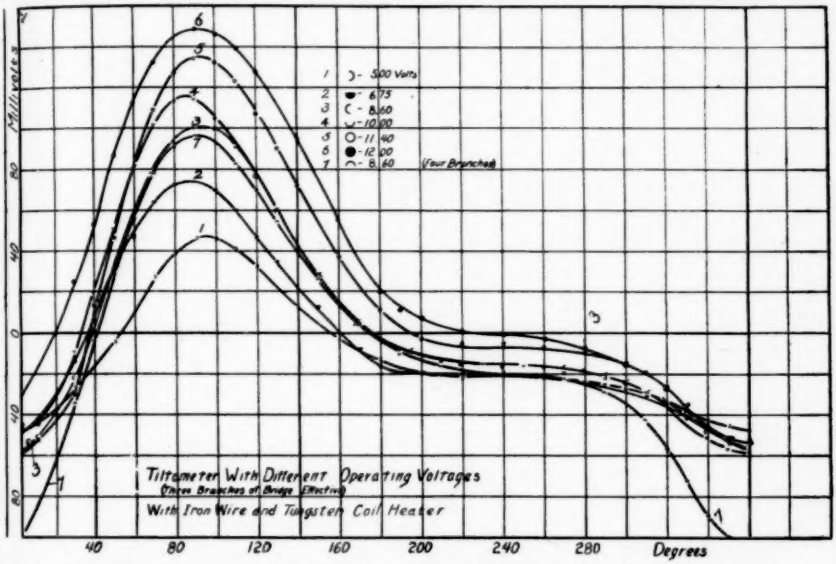

FIG. 7. *Deflection vs. rotation for a tiltometer with iron wire (.05 mm) for various heater voltages when bridge voltage is 5 V.*

values of voltage across the bridge and across the heater are indicated. The sensitivity increases both with the bridge voltage and with the heater voltage. The lower curves, *B* Fig. 6, show the effect of changing the bridge voltage and the heater voltage. In this case three branches only of the bridge are used. The fourth wire burned out and for it a resistance was substituted. This brings about an asymmetry in the curves. If the four branches instead of three had been effective here, the whole deflection, given by a rotation of 100°, would have been about 95 millivolts with a bridge and heater voltage of 3 and 7 respectively. The former still includes the drop across the resistance in series with the bridge.

A more extensive series of curves of a similar kind are shown in Fig. 7 for a tiltometer with iron wires of the same dimensions as those in the previous ones and with a tungsten coil heater. Here likewise only three wires were effective for all curves except 7. The bridge voltage was constant at 5.0 including the resistance drop. When the maximum deflection is plotted against the heater voltage the curve of Fig. 8 is obtained. The curve is a straight line within the range of this set of observations.

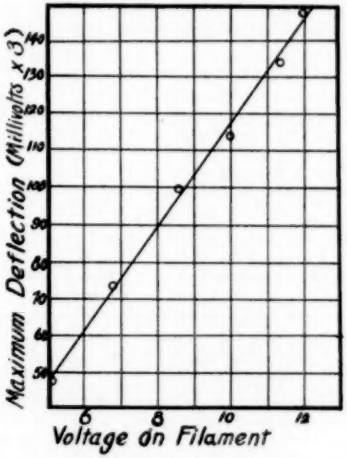

FIG. 8.—*Relation between heater voltage and maximum deflection. Data from curves in Fig. 7.*

APPLICATIONS

Such an instrument as has been described above presents some very striking advantages over other devices that may accomplish the same thing. The sensitive parts are totally and securely enclosed; there are no sliding electric contacts nor loose contacts of any kind, no making and breaking of circuits by switches with accompanying sparking. The sensitivity can be made very great and sufficient power may be put into it to operate relays. The use of the tiltometer may then be thought of in connection with any change of inclination out of the horizontal plane. A to and fro motion in the horizontal plane cannot be directly detected with the tiltometer. A mechanism to transfer this motion to motion about an axis other than the precisely vertical is required. The most striking application that suggests itself immediately for the tiltometer is on airplanes.

FIG. 9. *A tiltometer mounted for demonstration indicating a deflection of 60 on a uni-pivot galvanometer for a rotation or tilt of 15 degrees.*

Another application of interest is an "odograph." The "odograph" is an instrument suggested for use in the survey of highways and railroads. By means of it a record could be obtained of the general grade and smoothness of the road and of the change in the relative elevation of the two outer edges of the road. This should be a matter of interest and importance in modern highway and railroad practice. In fact such an instrument might become of interest to tourists. (Parenthetically it may be remarked that with a simple extension suggested by this a device may be made to record also the windings of the road. So that simultaneously the three characteristics, the winding, grade and twist of a road may be permanently recorded in absolute measure. These are data that are now obtained with much effort).

The various possible uses for the tiltometer may be classified as follows:

1.—Instruments to measure directly the tilt of surfaces.
Air plane inclinometer.
Odograph
Direction indicator for searchlamps.

2.—Instruments to measure velocity and pressure where tilting of a surface is incidently brought about.
Balances.
On scales for distant reading.
Densitometric instruments for gases and liquids.
Anemometer, etc.
Flow indicators.

3.—Instruments to measure distance where tilting of a surface may be used.
Height of ocean tides (tide recorder).
Depth gauge—contents of tanks for gases and liquids.
Delatometric instruments, etc.

4.—Relay or switch: e.g. a change in current through a circuit may be brought about without exposed contacts and without sparking.

We are giving a bibliography in a more extended paper on "The Transference of heat from and to fine wires, and some applications," which was presented before the Washington meeting of the American Chemical Society, 1924.

WIRE DIV., NATIONAL LAMP WORKS,
CLEVELAND, OHIO.

THE USE OF THE D'ARSONVAL GALVANOMETER IN RADIATION MEASUREMENTS

By Edison Pettit

The many advantages of the D'Arsonval galvanometer, including its constant zero, freedom from drift, and constant sensibility factor, are commonly thought to be offset by the lack of sufficient sensitiveness for radiation work. Our experience at Mount Wilson shows that this is indeed not the case, and that by the use of proper amplifying devices the sensibility can be pushed to a point that affords favorable comparison with the Thomson galvanometer.

D'Arsonval galvanometers with a resistance of 10 to 20 ohms and a sensibility of 3×10^{-10} amp/mm, when used at a scale distance of 8 meters, can be had on the market. Experience shows that with photographic devices this scale distance can be even increased to 12 or 16 meters, if the mirror is good, which will double its sensibility without loss in accuracy.

Fig. 1 shows the D'Arsonval galvanometer and registering device as used in conjunction with the vacuum thermocouple on Mount Wilson for stellar radiation measurements. A spectacle lens of 8 meters focal length is cemented to the case in front of the mirror of the galvanometer *G*. This mirror casts an image of the straight-filament lamp *F* upon the cylindrical lens *L* (half of a glass rod which has been sawed in two longitudinally) of the registering device *S*. This lens brings a portion of the image to a point focus upon the screw-driven photographic plate *P*. When the motor *M* is started this point traces a line on the plate.

Often it is desirable to use the galvanometer and registering device in a laboratory-room where it is not possible to secure dark-room conditions. The diagram in Fig. 1 shows the method devised to overcome this difficulty, which has been used for radiation measurements in tl e sun-spot spectrum. The cylindrical lens *L* in front of the moving plate *P* is replaced by the double horizontal slit *ss'* in the diagram below, consisting of two slits, 0.2 mm wide and 20 cm long, *s'* being about 1 cm in front of *s*. It is obvious that with this arrangement the only light which can reach the plate is a beam which lies in the plane defined by the two slits, and that the galvanometer mirror *m* must be in this plane. Since more light is needed, the straight-filament lamp is re-

placed by a 75-watt nitrogen-filled lamp, a straight portion of the image being projected upon the slit s' by the galvanometer mirror, although straightness is not important with so narrow a slit. "Process" or "Contrast" plates are used, the registering device being loaded by means of an opaque cloth. The apparatus is so placed that the slits do not face a window, white wall, or other considerable source of illumination. If the room is brightly illuminated, screens are placed at

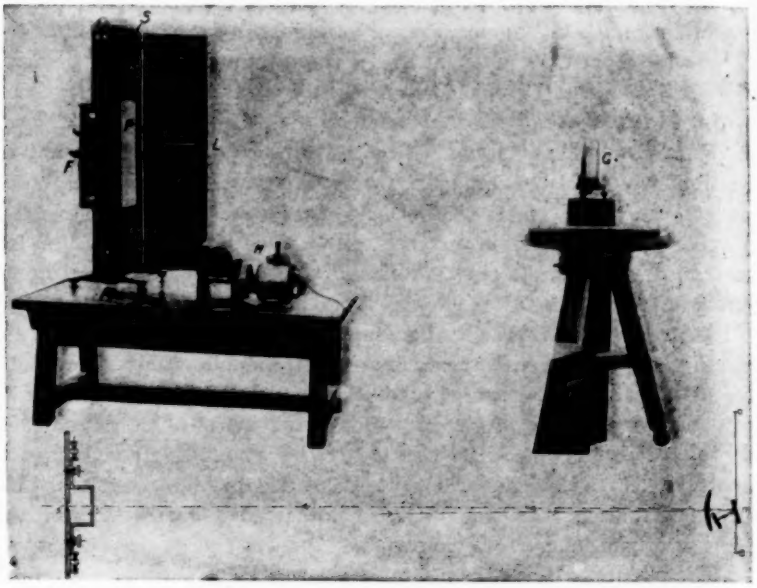

FIG. 1. *D'Arsonval galvanometer and photographic registering device. Below—Diagram of the optical system.*

either end of the slit and behind the galvanometer to reduce stray light. Under these circumstances a speed of three or four millimeters per minute in the moving plate can be maintained without fogging a slow emulsion.

Fig. 2 shows the vacuum thermocouple cell. We have used this type of cell with metallic calcium to maintain the vacuum for both thermocouples and piles. When spectral radiation measurements are being made, it is generally possible to place a short-focus lens of rock-salt, fluorite, glass or quartz behind the second slit of a spectrometer and bring the light which passes through this slit to a more or less diffuse

focus upon the receiver of a simple thermocouple, which gives larger deflections than a pile. When piles are used we have connected the junctions in series-parallel to give the maximum efficiency. The cell is arranged so that it can be shifted, causing the radiation to fall first on one junction, and then on the other, thereby producing a deflection of maximum value in the galvanometer.

Fig. 3 shows a set of deflections for the star Capella obtained in this manner. The light from the galvanometer mirror traces a broken straight line as the thermocouple receivers are interchanged upon the image at regular intervals. The photographic plate is placed on a suitable comparator and the separation of the two sets of parallel lines (indicated by the arrow) is measured.

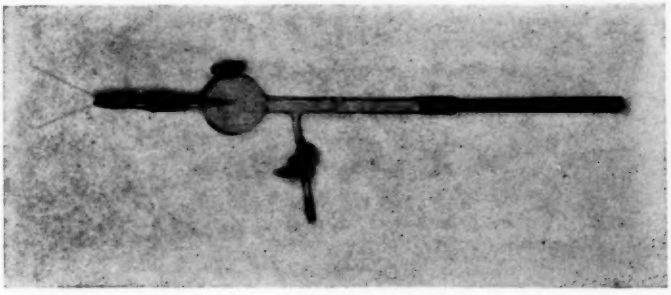

FIG. 2. *Cell used for thermocouples and thermopiles.*

Fig. 4 shows a two-screw comparator especially constructed for these measurements, with a deflection photograph K in position for measurement. The microscope M can be set in any position over a plate 8×18 inches. Both screws are of millimeter pitch and are read directly to thousandths. The dial D of the abscissa-screw, which is enclosed in a metal case, is read by a collimated microscope B. Self-aligning ball bearings are used for both screws in place of the usual solid bearings. Fast setting motion in abscissa is obtained by the motor m which operates at two speeds through the clutch C. When this clutch is thrown to neutral position the handle h can be used for rough settings. When fine settings are desired the pinion P is slipped to one side, which disengages the gear G on the end of the screw, leaving it free to be rotated by the fine-setting handle H.

Ordinarily the plate is set in the machine as shown in the illustration, the measuring of the deflections being done by the ordinate screw O,

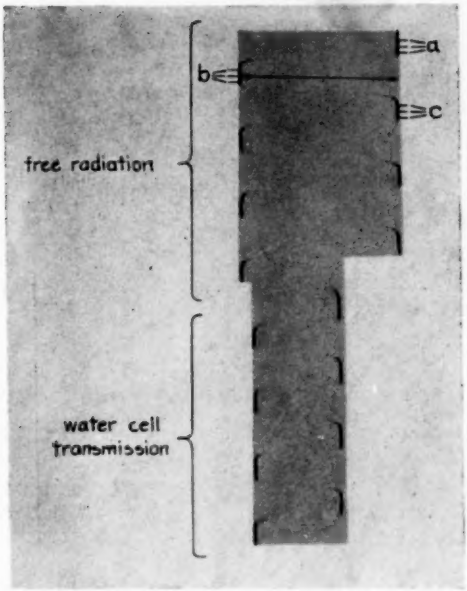

FIG. 3. *Photographic register of the galvanometer deflections obtained from the radiation from the star Capella.*

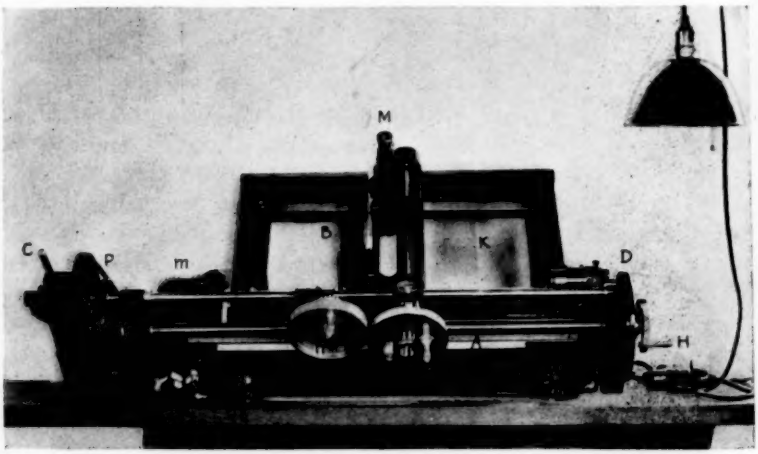

FIG. 4. *Comparator designed for the measurement of deflection-photographs.*

while the abscissa screw A is used to fix the point to be measured. The procedure is briefly as follows. The plate, on which deflections K occur at intervals of 1 cm, is set up in the machine with its edges parallel to the screws. A setting is made near the middle of the straight part of the first line a, Fig. 3, the microscope is shifted 2 mm in abscissa and a second setting made in ordinate. A third setting is made in a similar manner. The microscope is then shifted to a point one centimeter from the beginning in abscissa, and the points b are measured in a similar way. This process is repeated for c and all succeeding lines. The mean of the three settings in each case is then taken; and the first deflection, which is represented by the arrow, is obviously the difference between b and the mean of a and c. In this way the drift, if any, is eliminated.

The principal advantages of the photographic method, aside from increased sensibility, are the elimination of the effects of drift and the facility with which defective deflections can be discovered and eliminated. A study of the forms of defective deflection curves frequently leads to the discovery of the source of the disturbance in the observations.

That drift is effectively eliminated by the photographic method is illustrated by the following experiment. The self registering microphotometer[1] was used in which a vacuum thermopile, D'Arsonval galvanometer and photographic registering device form part of the apparatus. The lamp-current and slits were set to give a certain approximate deflection when a shutter was interposed between the lamp and the thermopile. Drift was produced in the galvanometer circuit by burning a pan of alcohol within a few feet of the thermopile and galvanometer. A set of eight deflections was then registered which was oriented at an angle of 14° to the edge of the plate by the drift of the galvanometer. This drift is much greater than is encountered in practice, the usual values seldom exceeding one or two degrees. The alcohol flame was extinguished and, the drift having ceased after the lapse of fifteen minutes, another set of eight deflections was registered which was oriented parallel to the edge of the plate. The two sets of deflections were measured as before described and both gave the same value, 38.85 mm. We have found that the mean probable error of measurement of stellar radiation for six observations of deflections of four or five centimeters is about 0.01 mm.

That so small a deflection as 0.06 mm has a real meaning when measured in this manner is shown in Table 1. A thermocouple was

[1] Astrophysical Journal *51*, p. 346; 1922. J.O.S.A. & R.S.I., *7*, p. 187; 1923.

arranged with registering device and galvanometer of the kind described above. A flashlight bulb was set at varying distances from the

TABLE 1.

Deflections observed	Deflections computed from inverse square law
4.89 mm	4.89 mm
0.90	0.88
0.41	0.44
0.19	0.20
0.06	0.06

thermocouple. A movable lens with pinhole diaphragm was used to form the image and shift it from one junction to the other. The table shows the results, the first column giving the measured deflections and the second column the values computed from the inverse square law on the assumption that the first measured deflection is free from error. A very satisfactory agreement will be noted, even when the deflection reaches the small value of 0.06 mm.

We may further increase the sensibility of the galvanometer by placing a fixed mirror close in front of the galvanometer mirror, thus causing the beam reflected from the galvanometer mirror to return to it for a second or third reflection (see diagram in Fig. 1). Each successive return of the beam to the galvanometer mirror from the fixed mirror increases the deflection two-fold, three-fold, etc., values forming an arithmetical progression. We have used as many as four reflections, which is a factor of five in the sensibility of the galvanometer. A limit is set by the widening of the image due to repeated reflections from the galvanometer mirror which is never a good plane.

With apparatus of this kind then, a deflection of 4 or 5 millimeters may be regarded as a large value. It frequently happens however, as for example, in spectral radiation measurements, that the range of intensities to be covered is very great, so that it may be desirable to measure deflections larger than the capacity of the registering device. In this case two lamps are used, so spaced that the images projected by the galvanometer mirror upon the registering device are separated by a distance somewhat less than the width of the plate being used. The registering device is then driven about one centimeter while the galvanometer mirror is on zero in order to get the spacing of the filament

images. For deflections larger than the width of the plate this spacing is added to the measured separation of the lines on the plate.

By the photographic method then, we have a factor of 100, and by use of the fixed mirror a factor of 3 to 4. If we may assume that a Thomson galvanometer can be read to 0.1 mm, the D'Arsonval galvanometer with these arrangements is then equivalent to a Thomson instrument with sensibility factor $i = 1 \times 10^{-11}$ amp/mm, and in actual practice the comparison is probably better than this.

MOUNT WILSON OBSERVATORY,
OCTOBER 30, 1924.

Electrical and Elastic Properties of Single Crystals of Zinc and Cadmium.—This is chiefly experimental work, although some attempt is made to interpret the results by the excessively difficult theories of the solid state developed by Grüneisen and Born. These metals were chosen because their atoms are arranged in hexagonal lattices, which suggests that the differences in qualities measured in directions parallel and normal to the axis of symmetry will be more pronounced than metals with cubic lattices display. Very long thin crystals were made by dipping a bit of a single crystal into molten metal through a hole in a superjacent mica sheet, and using it to draw a filament out of the molten mass; the orientation of the atom-layers all along the filament is expected to be controlled by the orientation of the layers in the crystal used to initiate the process. This is a common technique but the results are evidently not yet very certain or predictable. The authors produced several long thin filaments of Zn with the axis of symmetry of the lattice inclined to the axis of the filament at angles ranging from 3.6° to 88° and several of Cd with angles of 0° to 84° between the axes. Long thin crystals were desired so that Young's modulus could be measured by making them vibrate as rods clamped in the middle and measuring the frequency, and the resistance in the ordinary way for wires; the torsional rigidity was likewise measured by a static method. However it was impossible to measure a property such as conductivity for more than one direction (the axial direction) in each crystal; data for different directions always refer to different crystals, which is a grave drawback. This is illustrated, for example, by the data on resistivity as a function of the angle φ between the direction of current-flow (axis of the filament) and direction of crystal axis. The resistivities for 6 filaments of Zn with angles φ 3.6°, 4.7°, 21.9°, 56°, 81°, 81° were respectively 6.32, 6.32, 6.25, 5.99, 5.85 and 5.85, showing distinctly that the resistance tends to be greater the more nearly the current flows along the crystal axis. Putting $R = R_{\parallel} \cos^2 \varphi + R_{\perp} \sin^2 \varphi$ and adjusting $R_{\parallel}$ and $R_{\perp}$ to get the best agreement the authors obtain $R_{\parallel} = 5.83$ and $R_{\perp} = 5.39$ (reduced to 0° C. and expressed in microhms.cm), and for the ratio $R_{\parallel}:R_{\perp}$ 1.08

(for cadmium 1.19). These are smaller than the published values for Bi (1.36) and graphite (100); smaller also than the ratio of interatomic spacings in the two directions, 1.86 and 1.89. As the temperature is lowered $R_\perp$ decreases more rapidly than $R_\parallel$ so that the ratio rises; there is possibly an inverse change far down near 20° abs., to which the authors have penetrated but unfortunately with such scattered measurements that curves cannot be traced with confidence. Comparisons with data on polycrystalline wires of Zn and Cd indicate that the trend with T in one case (Cd) imitates that of $R_\parallel$ and in the other that of $R_\perp$, which seems curious. As for the measurements of Young's modulus E and the torsional rigidity T_0 they are used to calculate the best set of values for the 5 constants which, according to Voigt's crystallography, determine both. The data are then compared with the formulae for E and T_0 as functions of φ; the graphs indicate a good agreement for the form, less so for the latter; how much either agreement means is of course extremely difficult to say. It is interesting to note that Young's modulus varies in the ratio 7:25 for Zn (1:3 for Cd), the rigidity in the ratio 28:47 (18:24), the velocity of sound in the ratio 28:48 (24:37) as the orientation is changed. The theory proposed for the variation of resistance with direction of current-flow and with temperature is an involved modification of the idea that resistance must depend at low temperatures in exactly the same manner as specific heat upon the quantity Θ/T, where T stands for temperature and Θ for a constant of the material depending on the minimum wave-length of vibration possible to a cube of the material containing one molecule of atoms. Since the spacing of atom-layers differs along different directions the minimum wave length, and hence Θ and the temperature-trend of R may be expected to vary. If the theory proves to agree well with experiment it may be interpreted in terms of the vibrations of the atoms and their influence in facilitating or hindering conduction; but further calculation and much further experimentation are clearly required.—[E. Grüneisen and E. Goens, Reichsanstalt; ZS. f. Phys. *26* pp. 235-273; 1924.] KARL K. DARROW

Effects of Gas and of Heat Treatment upon sputtered platinum Films.—A large number of observations upon films of platinum sputtered in air, of various degrees of thinness as estimated from their resistances. The most striking result is that the resistances of the thinnest of the films decreased with increasing temperature; this is illustrated by a reproducible descending straight line curve for a particula r film; after the film had been heated in the presence of oxygen for awhile, the resistance was found to increase linearly with temperature instead of decreasing. Sometimes oxygen in contact with a sufficiently hot film causes its resistance to rise suddenly and rapidly to an extremely high value from which it does not return; the author thinks that the oxygen, combining with the hydrogen occluded in the film into water vapor, ruptures the film mechanically.—[F. W. Reynolds, Cornell; Phys. Rev. *24*, pp. 523-531; 1924.] KARL K. DARROW